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DENVER AIR POLLUTION STUDY - 1973
Proceedings of a Symposium
Volume I



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DENVER AIR POLLUTION STUDY - 1973

Proceedings of a Symposium

Volume I

Edited

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INTRODUCTION

The Denver Urban Plume, often referred to as the "brown cloud," is one of the area's most aesthetically displeasing features. Although the brown cloud was observed in the early 1950's, its occurrence and severity have increased with the city's rapid population increase and urban development. It is usually associated with the Northeast section of Denver, where there is a concentration of industries, railways, freeways and a major power plant. During the late fall and winter months, when severe temperature inversions occur during periods of low wind speeds, the visible and olfactory characteristics of the cloud are easily noticed by residents throughout the metropolitan area, particularly along the South Platte River basin.

For a number of years, the composition of Denver's Urban Plume was unknown, and it became obvious that its control was impossible without a detailed study to determine its particulate and gaseous composition, and the influence of meteorological conditions. In November 1973, a coordinated effort was initiated by the U.S. Environmental Protection Agency to investigate Denver's brown cloud. Participants in the study included:

1. Atmospheric Aerosol Research Section, Atmospheric Chemistry and Physics Division, Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, N.C. (AARS-EPA)
2. University of Denver, Denver Research Institute (DRI)
3. Loren Crow, Consulting Meteorologist
4. Meteorology Research, Inc.
5. Meteorological and Air Pollution Control Commission, Colorado State Board of Health (CSBH)
6. Region VIII, U.S. Environmental Protection Agency
7. National Oceanic and Atmospheric Administration (NOAA)
8. National Center for Atmospheric Research (NCAR)

9. General Motors Research Laboratories
10. University of Washington
11. University of Texas
12. Thermo-Systems, Inc.
13. United States Army, Rocky Mountain Arsenal
14. Battelle Columbus Laboratories
15. IIT Research Institute

About fifty samplers of several different types were used to collect over 500 aerosol samples, and several types of gaseous testing equipment were used at nearly ten different locations. Meteorological data were collected at all the field laboratories and at other sites in the greater Denver area. Some of the extraordinary research conducted during the investigation included air pollution measurements from an instrumented aircraft; LIDAR observations conducted by NOAA; non-particulate organic contaminants analyzed by Battelle; radiation measurements made by NCAR; and non-volatile particulate analyses, using scanning electron microscopy/energy dispersive X-ray spectrometry, conducted by the Structures Laboratory of DRI.

Prior to the research activities, DRI was active in coordinating the preliminary efforts with EPA and the State of Colorado, in establishing monitoring sites and the sampling networks, and furnishing logistic support. During the investigation, DRI maintained the air pollution alert system, continued the logistic support, and operated its own environmental laboratory in the field.

In June 1974, preliminary results of many of the studies were published as preprints for the Air Pollution Control Association meeting. Only preliminary results were reported because of the early date required for publication and restrictive page limitations.

In March 1975, DRI, through an EPA grant, conducted a three-day symposium; comprehensive research reports from the Winter 1973 Denver Urban Plume Study were presented. Volume I is the first of two volumes that contain the proceedings of the symposium. DRI was responsible for editing. Volume II will be published at a later date.

AIRFLOW STUDY RELATED TO
EPA FIELD MONITORING PROGRAM
DENVER METROPOLITAN AREA
NOVEMBER, 1973

Loren W. Crow
Consulting Meteorologist
Denver, Colorado 80210

ABSTRACT

This paper describes the detailed hourly airflow, both at the surface and at elevations above the surface, related to air pollution episode days in Denver, Colorado, during November, 1973. Progressive stages of the depth of the well-mixed layer near the ground are documented. A near reversal of airflow on the more dense air pollution days is a repeatable phenomenon. Rapid dispersal sometimes occurs when strong winds assume control and move the polluted air rapidly away from the city. There is a tendency for the "heat island" to develop a "chimney effect" which carries effluents away from the metropolitan area at a level above the ground to the north-northeast of Denver.

INTRODUCTION

This report covers a summary of airflow patterns related to several air pollution episodes during November, 1973. This report will emphasize data collected for November 14, 16, 17, and 21. The sponsoring agency was the Atmospheric Aerosol Research Section, Chemistry and Physics Laboratory, Environmental Protection Agency, National Environmental Research Center - Research Triangle Park, North Carolina. The author assisted in selecting appropriate days for concentrated collection of air samples throughout the Denver metropolitan area. It was also his responsibility to coordinate the collection of wind data by use of pilot balloon (pibal) ascents at three locations on sampling days and to collect a photographic record from advantageous points throughout the city.

This airflow study adds to the body of data previously collected during special study periods^{1,2,3,4,5} in the Denver metropolitan area.

DATA SOURCES AND THEIR LOCATION

The geographic area of greatest concern for air pollution in the Denver metropolitan area is primarily a segment of the Platte River drainage extending from a few miles south-southwest to a few miles north-northeast of the city center. The map shown as Fig. 1 identifies most of the data collection points used in this study. The area shown covers approximately 25 miles square. The Atomic Energy Commission's facility at Rocky Flats, which is operated by Dow Chemical Company, is located at the northwest corner of the map. The town of Henderson is near the northeast corner and the Arapahoe County Airport is near the southeast corner.

Two elevation contour lines, one at 5200 feet and the other at 5500 feet, indicate the downward slope of the terrain on both shoulders of the Platte River drainage. Although not shown, a 6000-foot contour line runs near the west edge of the map. There is a minor drainage basin along Sand Creek, which runs from just west of Buckley Air National Guard Base (ANGB) toward the northwest past Stapleton. The surrounding terrain features help influence wind directions within that small drainage basin. Also, the combination of Clear Creek which drains from the mountains near Golden toward the northeast, and Ralston Creek which drains from the northwest toward Arvada, helps influence local windflow patterns in that portion of the metropolitan area.

The locations where pibals were released are identified at the cross points in the seven-point vertical scales at Arvada, Yellow Cab, and the EPA Trailer site. The major highways and thoroughfares which are shown carry a major portion of the automobile traffic in the metropolitan area.

Since early 1965 Denver has been one of the cities where air pollutants are being measured in the Continuous Air Monitoring Program (CAMP). Denver's station is located at 2105 Broadway.

The types and frequency of observations and photographs collected are indicated in Table I. Data for four days are being emphasized.

IMPORTANCE OF AIR STABILITY

When strong winds prevail in the Denver metropolitan area there is near complete ventilation and a horizontal transport of air moving into the city from one side and out and away from the city on the opposite side. This type of ventilation occurred on November 14 and 21, 1973. On November 14 ventilation occurred as air moved away from the city

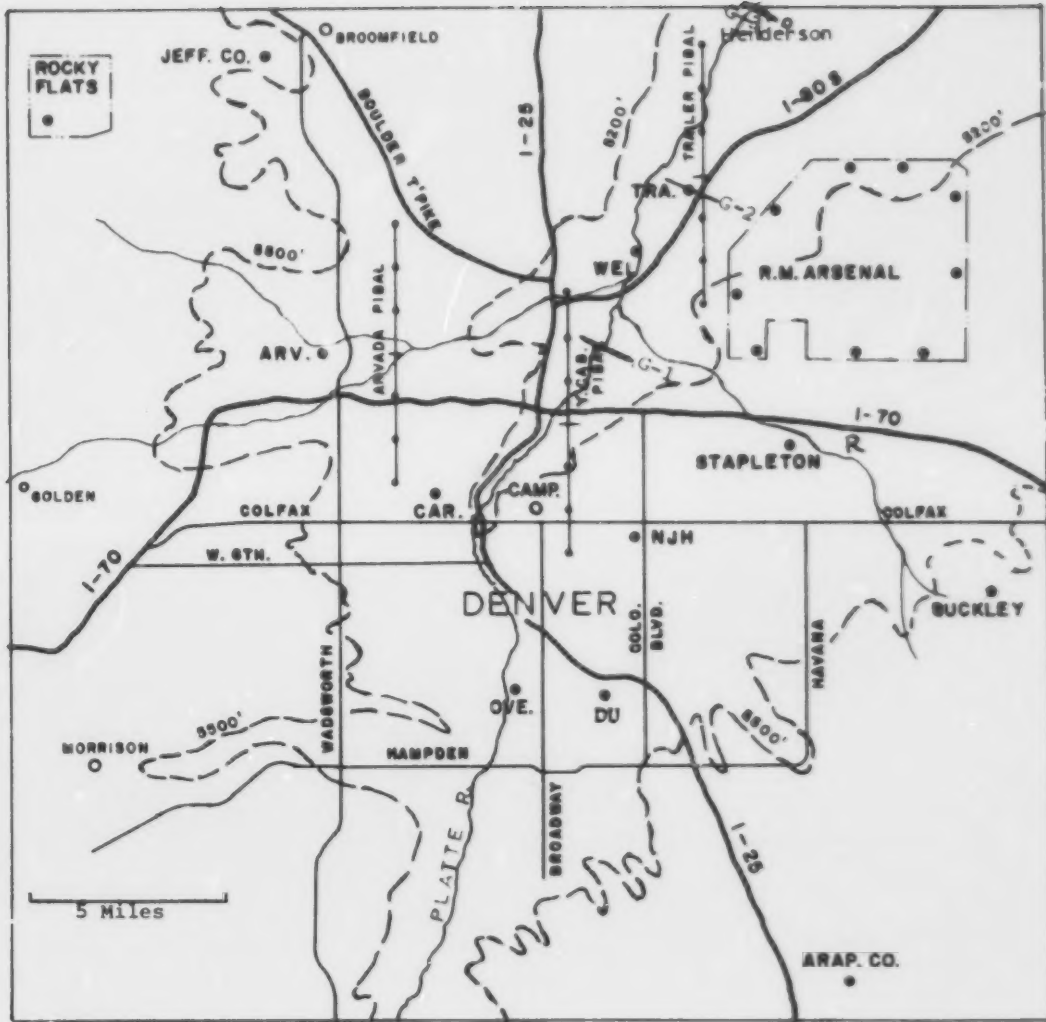


Fig. 1. Identification map.

Table 1. DATA INDEX OF METEOROLOGICAL AND PHOTOGRAPHIC DOCUMENTATION COLLECTED FROM MULTIPLE SOURCES IN THE DENVER AREA BY LOREN W. CROM AS PART OF THE EPA AIR POLLUTION STUDY FOR NOVEMBER, 1973.

	Nov.	6	7	9	10	14	16	17	20	21	24	29	30
PIBALS													
EPA Trailer { # runs--		6	6	5									
Yellow Cab { 0900 to		10	12	12									
Arvada { 1500													
RAWINSONDES													
Stapleton AP # runs		2	a.m. only	3	a.m. only				2		2	2	2
SURFACE WINDS													
Airports # hours													
Stapleton 24		x	x	x	x	x	x	x	x	x	x	x	x
Buckley 24 plus		x	x	x	x	x	x	x	x	x	x	x	x
Jeff. Co. 17		x	x	x	x	x	x	x	x	x	x	x	x
Arap. Co. 17 temps.		x	x	x	x	x	x	x	x	x	x	x	x
Rocky Flats 24		x	x	x	x	x	x	x	x	x	x	x	x
Arsenal 24		x	x	x	x	x	x	x	x	x	x	x	x
(set of 9)													
State Health 24													
Welby		x	x	x	x	x	x	x	x	x	x	x	x
Arvada		x	x	x	x	x	x	x	x	x	x	x	x
CARIH		x	x	x	x	x	x	x	x	x	x	x	x
NJH		x	x	x	x	x	x	x	x	x	x	x	x
Overland		x	x	x	x	x	x	x	x	x	x	x	x
EPA Trailer (partial)		4	9	10	17	10	24	16	x	17	12	x	x
PHOTOGRAPHS													
Aerial - 80 min. flights		1020-1140		1120-1240						1040-1200			
Time-lapse													
Fed. Center to NE		x	x	x					x	x	x	x	x
Buckley to NW									x	x			
35mm slides													
EPA Trailer 4 dirs.			x		x								
Rocky Flats 3 dirs.		x	x	x					x	x	x	x	x
Sheraton Hotel 2 dirs.				x					x	x	x	x	x
L. W. Crow Misc.		x	x		x				x		x		
SURFACE TEMPERATURES													
Various business firms		x	x	x					x		x	x	

toward the east. On the 21st the city was ventilated by air moving rapidly from east toward west. An illustration of such ventilation is shown in the upper portion of Fig. 2.

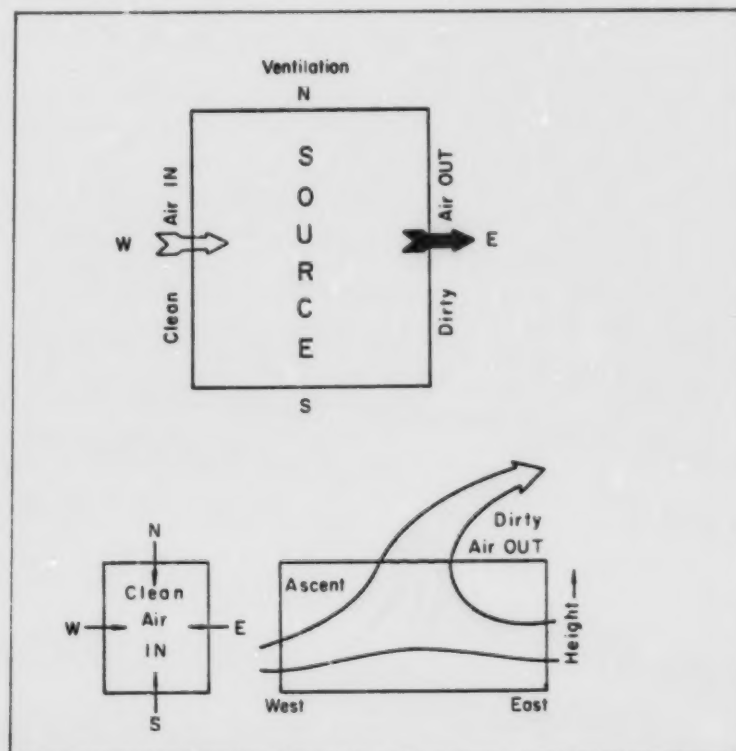


Fig 2. Sketches of two alternate paths for cleansing mechanisms.

The transport of air pollution, both from elevated sources, ground sources, line sources, and area sources, is highly dependent on the stability of the layer of air into which they are introduced. Elevated plumes emanating from sources near the southern edge of the metropolitan area can often be identified moving toward the north in ribbon-like plume patterns. Each individual plume reaches its effective stack height soon after being emitted from the source. As the plume moves downslope it assumes an elevation somewhere between the initial elevation above the ground and a continuing constant elevation with respect to sea level.

A compound plume of pollution can be formed by several individual elevated plumes. A similar compound plume can also be produced as a layer of pollution is raised above the ground level as it passes over

the heat island of concentrated buildings and/or highways near the center of a city. Heat from the burning of 200,000 to 400,000 gallons of gasoline during daily rush hour traffic periods helps to expand the heat island. Much of the polluted air ascends to the upper part of the heat island and then travels horizontally downwind at some layer above the ground to the north-northeast. This combination of upper level outflow is illustrated as a chimney effect in the lower part of Fig. 2. Such a mechanism of outflow is fed by a net inflow toward the center of the metropolitan area near the surface during early forenoon hours. An earlier study⁵ found the net inflow rate to be approximately one-half mph toward the center of the city.

During forenoon hours it is often possible to identify separate layers of pollution. A polluted layer of air having a local source near the ground can often be separated from an elevated pollution plume by a non-polluted layer of clean air between.

The early morning temperature profiles from the 0500 Stapleton Airport rawinsondes in the lowest 1500 feet are presented in Fig. 3. The sloping dashed lines indicate the dry adiabatic lapse rate and the depth of well mixed air which can be estimated for the times shown, based on the subsequent surface temperature observations made during the forenoon at Stapleton Airport. The upper portion of the 0500 temperature profile would have been abruptly changed at the time of cross-city ventilation near noon on November 14 and November 21.

Using an approximate composite of the 12 low level a.m. soundings, the corresponding resultant patterns of pollution layers can be estimated. Three schematic diagrams which illustrate the influence of stability factors are shown in Fig. 4. Under stable air conditions each individual elevated plume moves off horizontally at its effective stack height with no mixing to the ground until surface heating is able to mix the layer up to and including the height range of that particular effective stack height above the terrain over which the plume was moved. This is illustrated in Part A of Fig. 4.

In Part B of Fig. 4, a comparative estimate is made of the temperature profile as it would occur within the heat island segment of air near the north edge of the downtown portion of the city. The influence of the heat island does not eliminate the air stability, but it can produce an elevated compound plume for visible pollutant materials moving farther downwind beyond the main portion of the heat island area.

In Part C of Fig. 4, indication is given as to how the top of a visible polluted layer emanating from ground sources increases as surface temperatures increase during forenoon hours. When the air mixes upward through sufficient depth to envelop the previously identifiable plumes, separate layers can no longer be distinguished.

The nearly repeatable pattern of pollution over Denver on episode days is illustrated in the cross-section diagram of Fig. 5. This

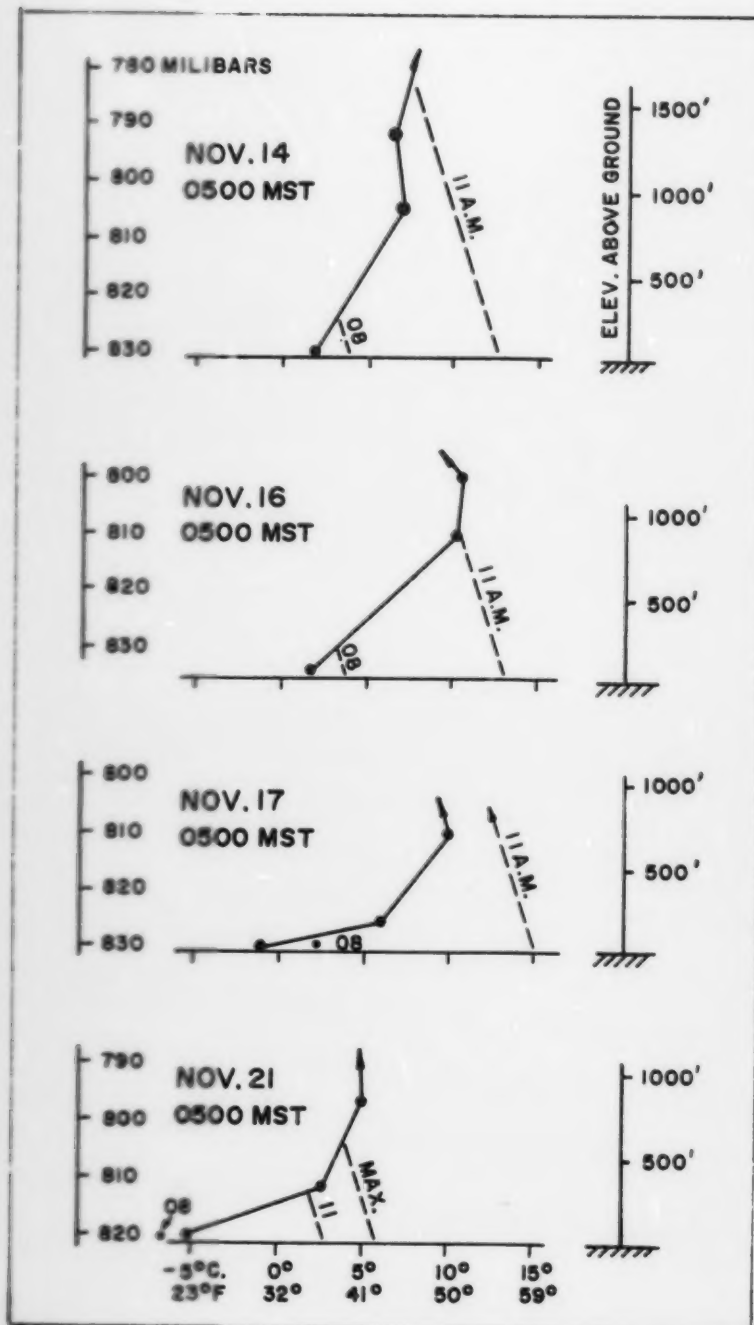


Fig. 3. Early morning temperature profiles for four pollution episode days during November, 1973, as measured by rawinsonde at Stapleton Airport.

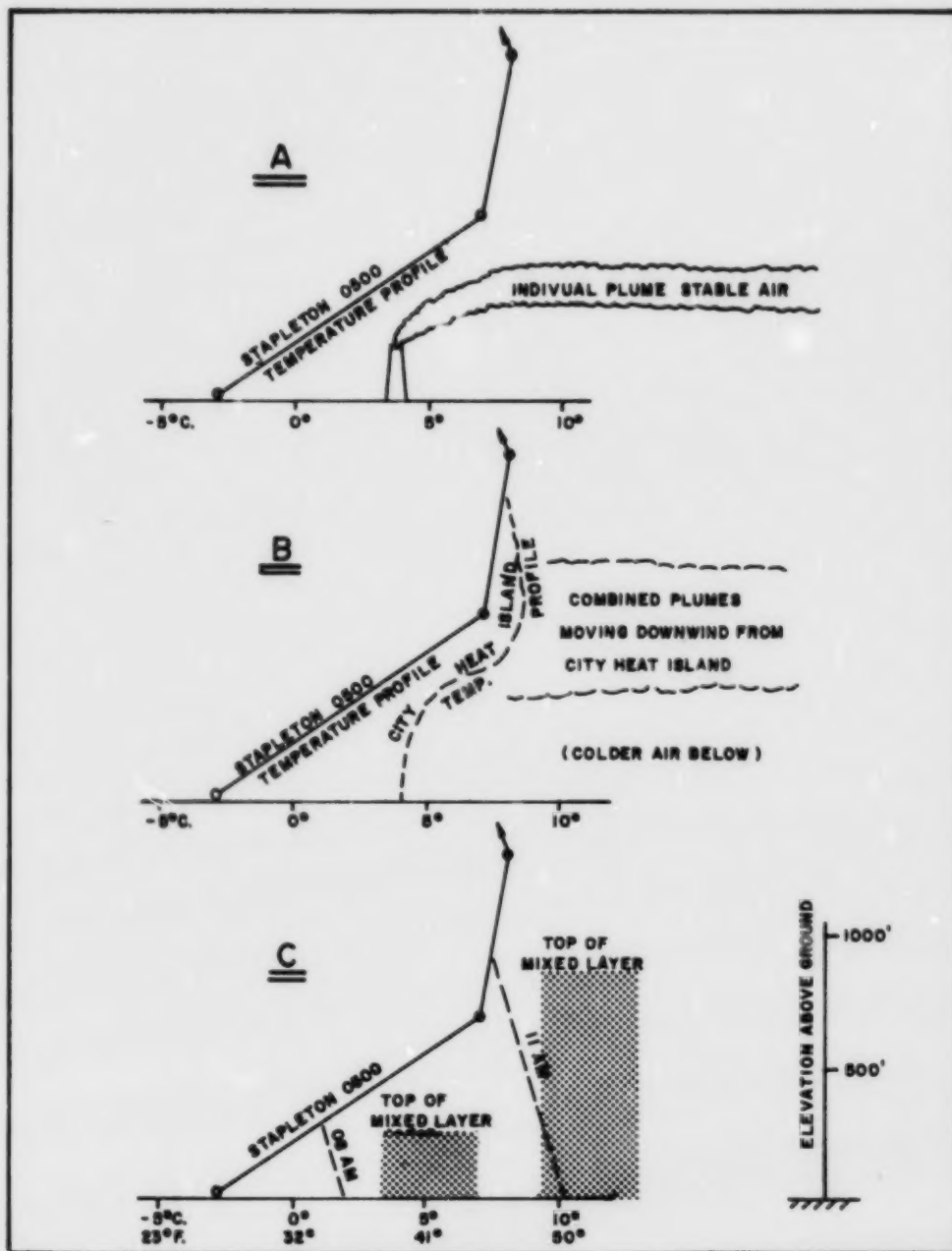


Fig. 4. Relationships of temperature profiles and polluted layers for: A. elevated source moving horizontally at effective stack height in stable air; B. city heat island effect producing elevated combined plume in stable air; C. comparative tops of polluted layer from ground level sources with increasing surface heating during forenoon hours.

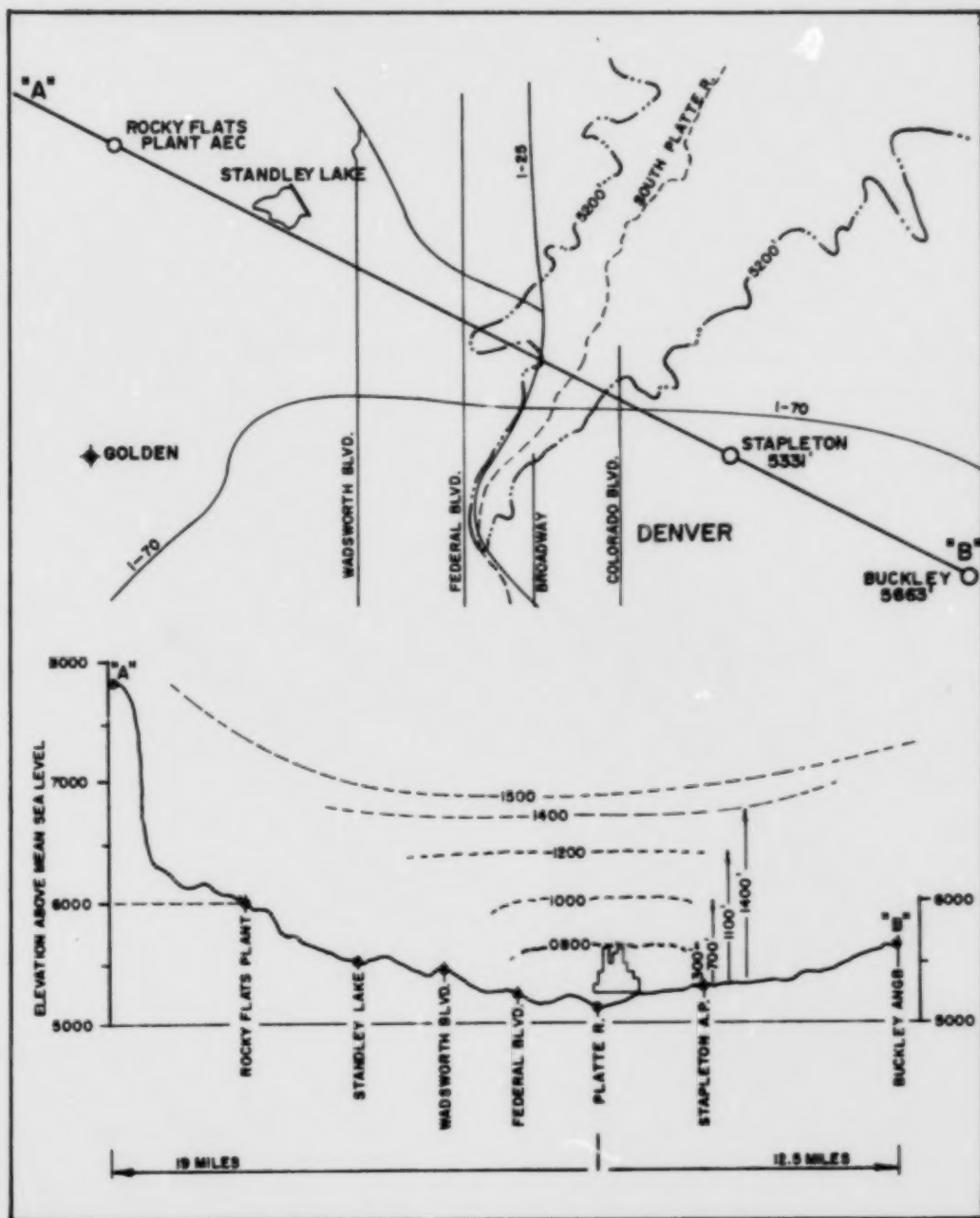


Fig. 5. Typical WNW-ESE profile of pollution layer depths over metropolitan Denver between 0800 and 1500 on days when temperature inversions are not eliminated.

cross-section has been prepared to show the vertical profile of terrain and the pollution layer at various hours of the day as it is typically observed. The profile, which is greatly distorted in the vertical scale, runs from the mountainous area to the west-northwest of the Rocky Flats Plant southeastward to Buckley ANGB. This profile crosses the Platte River about three miles northeast of the downtown City of Denver and passes through Stapleton Airport. Multiple photographs, taken during the special study period of November, 1973, and during other periods studied by this author, support the approximate elevations of the polluted layer tops as shown in the cross-section for the hours from 0800 through 1500. At both 0800 and 1000 the heat island effect pushes the upper boundary of the polluted layer somewhat higher over central Denver. The polluted layer depths should be considered typical of days in which the temperature inversion is NOT broken. In the summer months the respective tops of the polluted layer may be slightly higher.

The ground level for most downtown buildings is approximately 5200 feet above mean sea level. The higher buildings extend slightly more than 400 feet above ground level. Thus, they extend approximately 270 feet above the runway elevation for Stapleton Airport, which is 5331 feet. The elevation of the polluted layer tops is shown as above ground level at Stapleton Airport since the surface temperatures used to help derive the elevation tops are those measured hourly at the airport. Temperature profiles from the 0500 rawinsonde at Stapleton have been used to support the findings shown in Fig. 5.

Although not shown in this cross-section the sequence of air motion changing from downslope to upslope between 0800 and 1500 must be considered in estimating the top of the polluted layer. The most frequent direction of smoke layers as seen by the weather observer at Stapleton Airport is to the southwest through north. There are relatively few instances when the observer indicates that either smoke or haze is observed in all directions from his point of observation.

The most frequent pattern of spreading for the pollution layer from noon through 1500 is to the south and/or west of the downtown area. This is aided by upslope motion above the higher terrain located in that direction from the city. For instance, North Table Mountain, South Table Mountain, and Green Mountain all extend above 6000 feet MSL. At the tops of these relatively flat protrusions the layer of stable air in early morning hours is very thin. Thus, a small amount of surface heating is required to eliminate the stable air layer. The stable layer is replaced by air which is well mixed vertically. In some instances a chimney-like airflow pattern is produced. Air which is heated and rises above the low foothills may move back toward the east above the temperature inversion over the valley. This upward motion of air above the higher terrain where the temperature inversion has been eliminated induces a movement of air coming first southward and then westward from the downtown area of Denver. Before it reaches the mountainous terrain, vertical mixing often has destroyed the temperature inversion, and the upper edge of the polluted layer becomes quite diffuse.

The top of the polluted layer is best characterized as having small undulations rather than being absolutely flat. An instantaneous photograph often makes it appear as quite level but time-lapse photography shows variations in the upper level.

The frequency with which the western edge of polluted layer reaches Rocky Flats is less than one-third of the days when relatively dense pollution can be noted in the downtown area of Denver. Likewise, there are very few instances when the polluted layer envelops Buckley ANGB.

When a layer of pollution extends over the downtown area it correspondingly decreases the rate at which surface heating can be produced by solar radiation. Therefore, by the early afternoon hours it is generally true that the surface temperatures are cooler under the polluted layer than in the surrounding terrain where clearer air has permitted more rapid surface heating. Thus, the profile pattern of Fig. 5 shows the outer edges of pollution to be somewhat higher during afternoon hours. The higher ground surfaces above mean sea level near the outer rim of the basin, especially to the south and west of Denver, also help to support an earlier elimination of the temperature inversion with the same amount of solar radiation.

Although the peak density near the ground occurs most frequently near the end of the morning rush hour period for sampling stations near the center of the metropolitan area, the deepest layer of visible pollution generally occurs between noon and 1500. The aerial photograph presented as Fig. 6 was taken November 9, 1973, at approximately 1200 from an elevation of 7000 feet. The layer of pollution extends approximately 1100 feet (335m) above street level in the center of the city at that time. An abbreviated record of a typical airflow reversal day, November 9, is shown in Fig. 7. There was downslope drainage at 0300, upslope reversal at 1100, and stable conditions at both 0500 and 1200.

DETAILED POLLUTION EPISODE PERIODS

The following episode periods have been examined to determine the airflow patterns both near the surface and through several hundred feet above the surface. The stability has been determined by temperature profiles obtained from the Denver Airport rawinsonde with some supplemental aircraft soundings. Individual hourly maps of surface winds show a high variability of airflow at different times for each day.

Pibal runs were made on an hourly basis at the EPA Trailer during daylight hours beginning at 0900 on most episode days. At the other two locations pibal runs were made each half hour beginning at 0900. At all three locations theodolite readings were made at 150-foot intervals along the vertical ascent path.

In addition to the fixed time photographs which were taken from various places throughout the city, an additional record of the changes in visible pollution layers was obtained using time-lapse camera

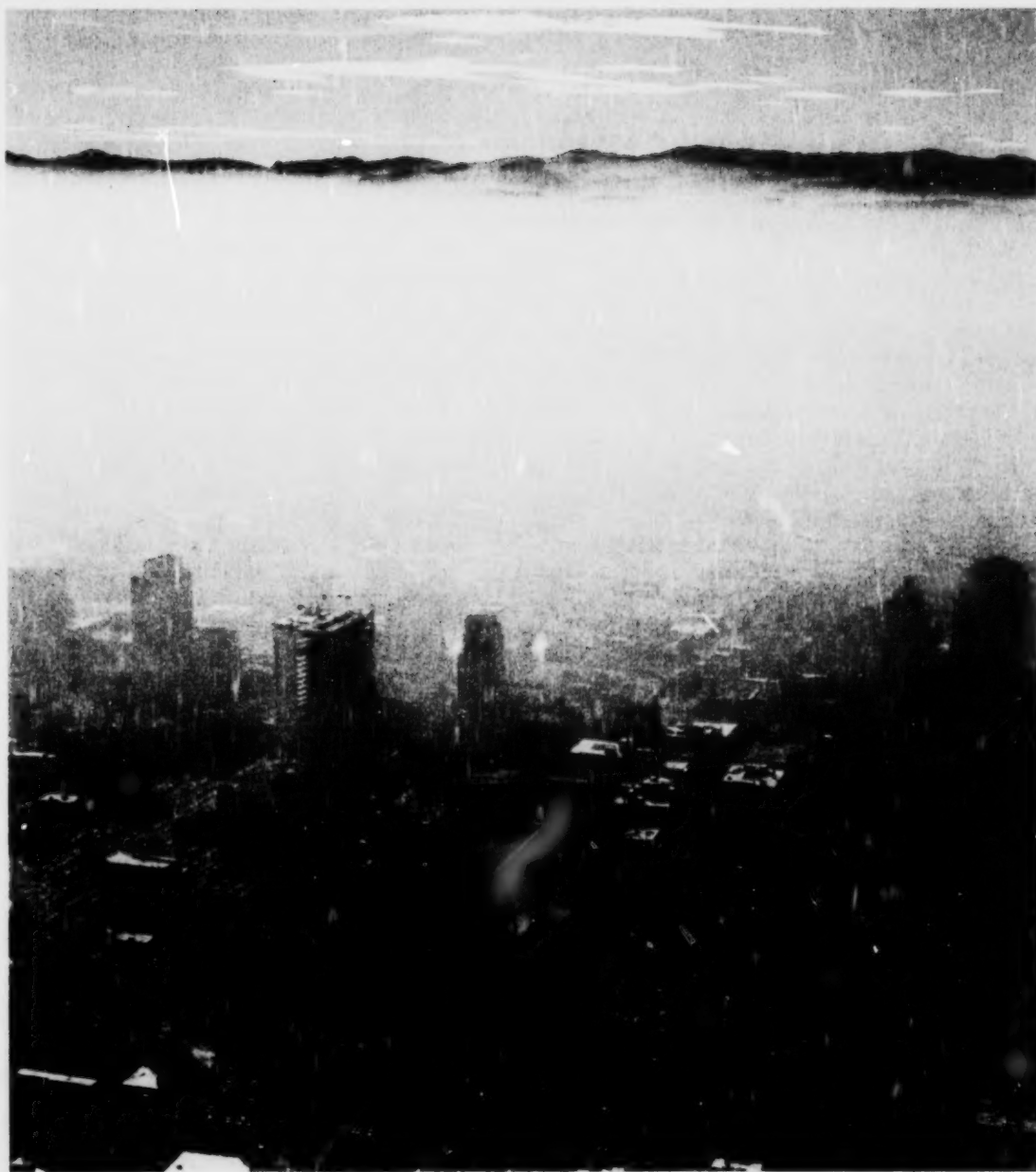


Fig. 6. Aerial photograph from aircraft at 7000 feet MSL near noon on November 9, 1973. Scene is toward the southwest.

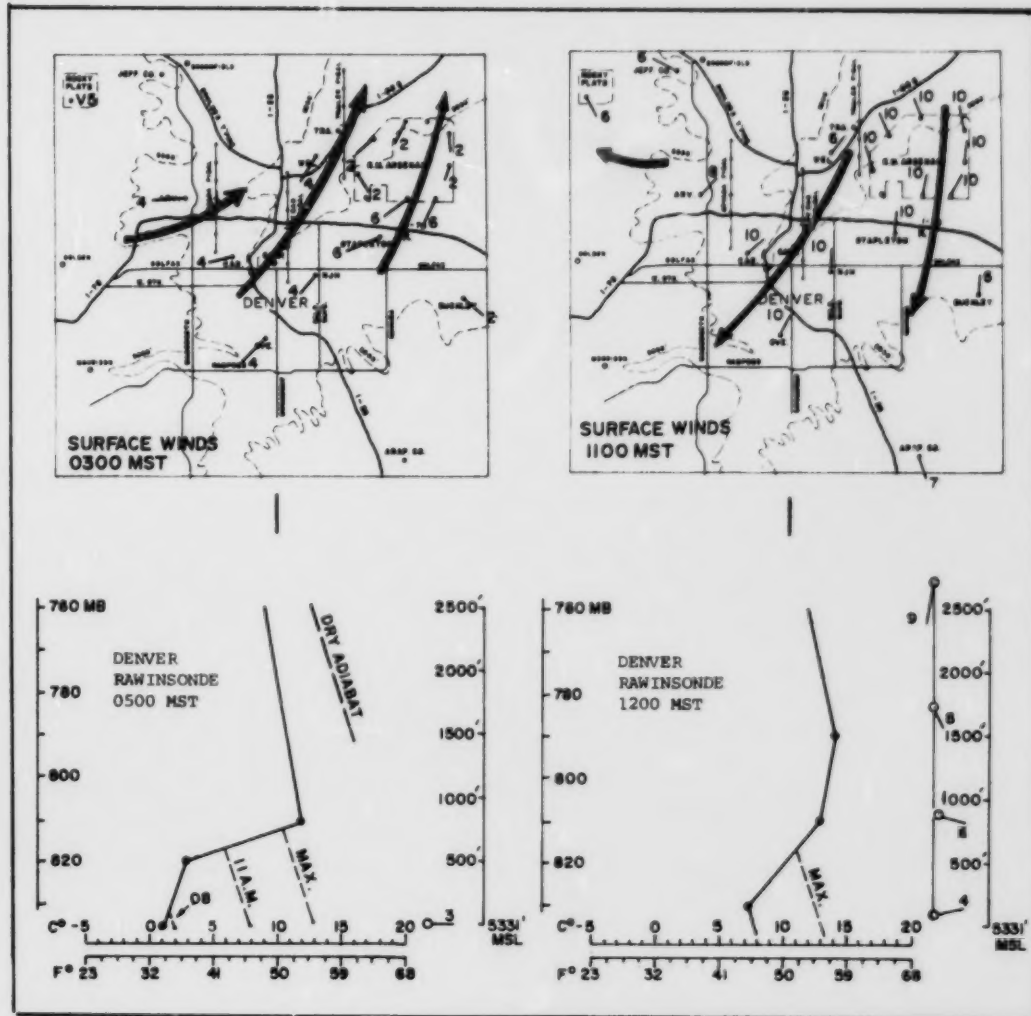


Fig. 7. Example of surface airflow patterns during: a. nighttime downslope converging drainage flow at 0300, and b. daytime upslope flow at 1100 on November 9, 1973. The temperature inversions was not broken that day.

techniques. One camera, using Super 8 film, took pictures from the 13th floor of the Bureau of Reclamation Building located near the west edge of the metropolitan area. The second camera, using 16 mm film, took pictures from the roof of a hanger located at Buckley ANGB.

Episode Day November 14

The day of the 14th was forecast to be a relatively light air pollution day. However, it was the first day that aircraft sampling facilities became available and wind measurements were made to fit with the aircraft measurements.

During the early forenoon hours the air pollution buildup was typical for a weekday morning. However, the temperature inversion which existed at 0500 was eliminated before noon and the layer of air near the surface was mixed with strong synoptic airflow from the west-northwest. Synoptic linkage occurs when the pressure airflow identifiable on synoptic weather maps is sufficiently strong to override all local terrain control features.

One photographic record of the air mass changes that occurred shortly before 1100 on November 14 was obtained from the observing site on the eighth floor of the Sheraton Inn-Denver Airport. A set of before and after photographs is shown in Fig. 8. The scene at 0900 toward the northwest shows a relatively dense layer of pollution in the north portion of Denver. The lower photograph in Fig. 8 shows markedly improved conditions for the same scene.

A set of three photographs taken to the west of the EPA Trailer also helps document a sharp change near 1045. The time of these three photographs is 0930, 1022, and 1100. Note the sharp change in improved visibility between 1022 and 1100 shown in Fig. 9.

The time-lapse photography at Buckley ANGB also confirmed the rapid change which took place as the pollution layer was moved away from the city toward the east.

A set of 13 stations was used to plot same-hour winds to show airflow patterns near the surface in the Denver metropolitan area. The sequential order of the wind measuring stations used is shown in Fig. 10.

The first six stations are on the left shoulder of the Platte River with the Overland and Welby stations being very near the river. Only three of the nine observation points within the Rocky Mountain Arsenal are listed. The seven stations on the right shoulder are arranged sequentially from lowest toward highest elevations.

The hourly sequence of airflow at the 13 stations shown in Fig. 11 illustrates the abrupt change which took place between 1000 and 1100

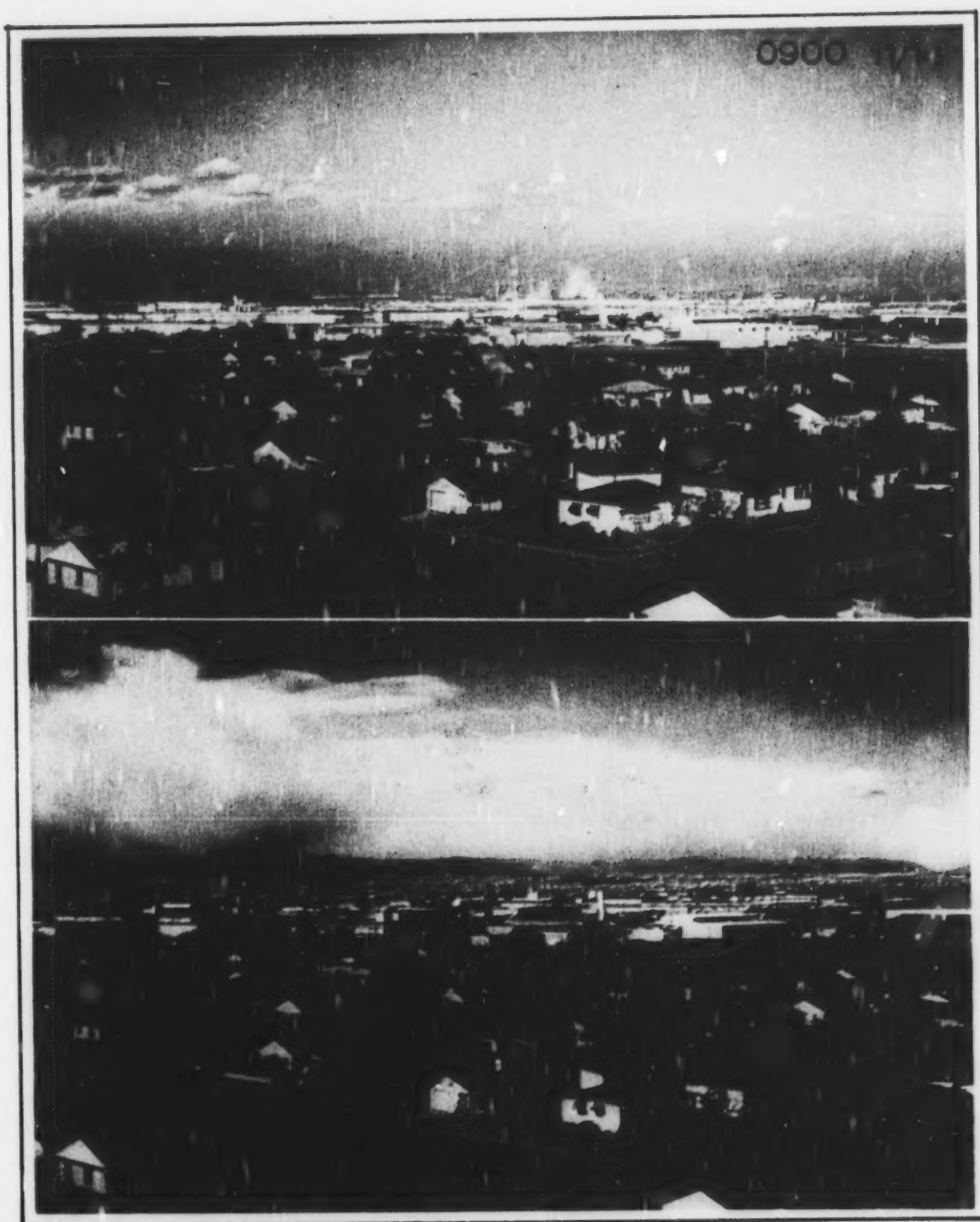


Fig. 8. Contrast between polluted air on a weekday morning and same scene at noon following one hour's linkage with synoptic airflow from west to east and elimination of the temperature inversion, November 14, 1973.

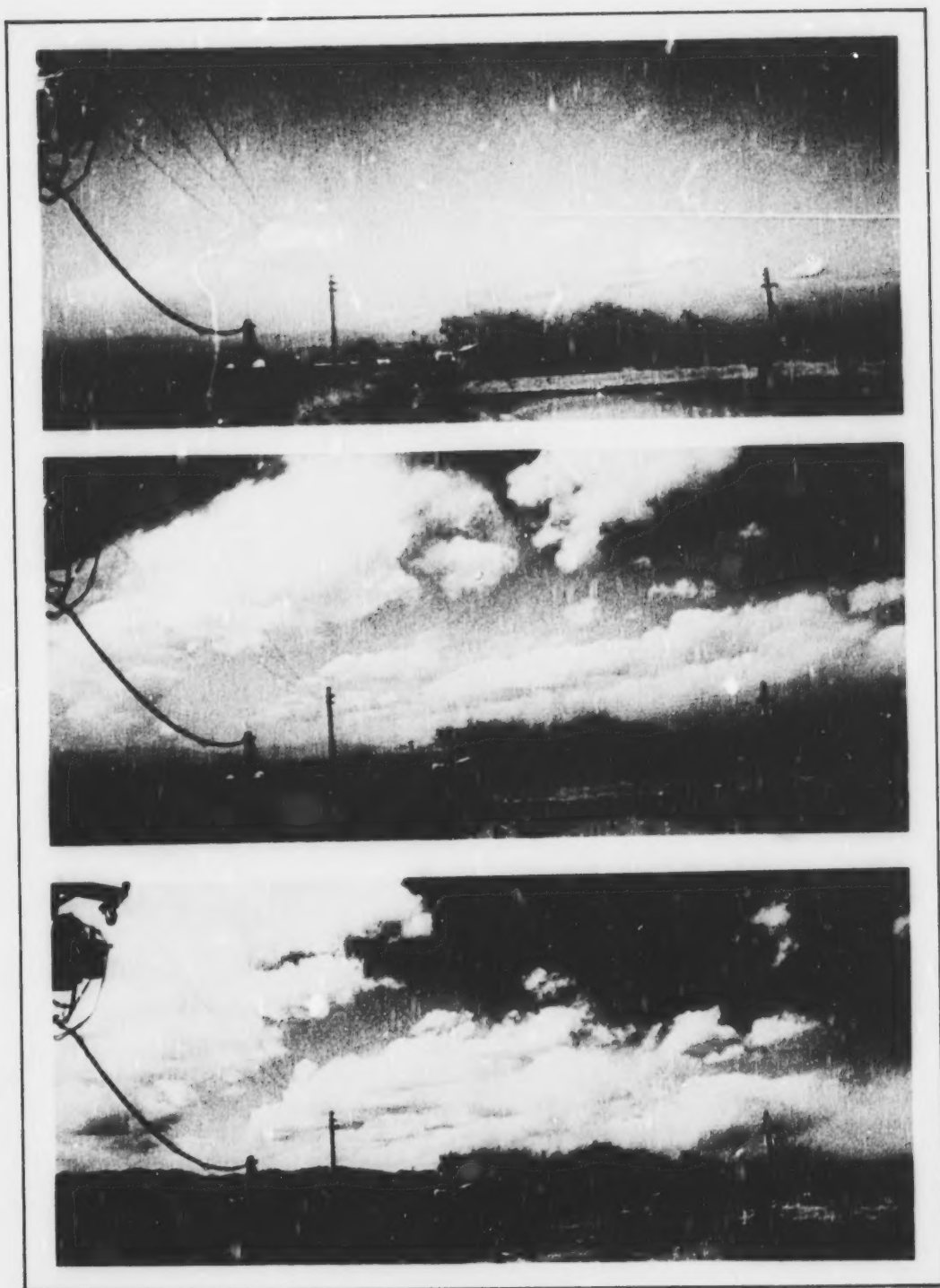


Fig. 9. Sequential photographs looking west from EPA Trailer during forenoon of November 14, 1973.

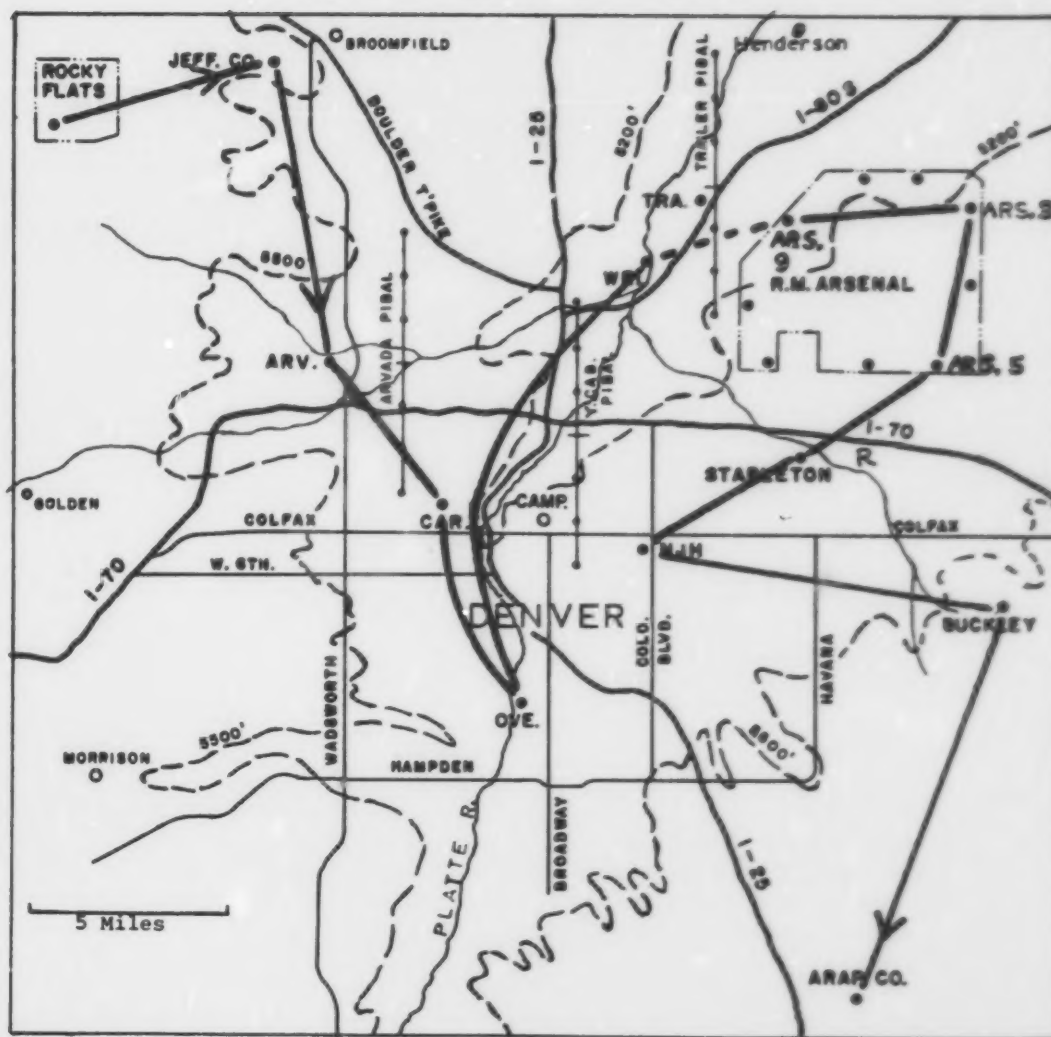


Fig. 10. Sequential order of thirteen wind measuring stations for which hourly data are used to identify airflow patterns. Left shoulder of Platte River includes six stations from Rocky Flats through Welby. Right shoulder group includes stations from ARS. 9 through Arapahoe County.

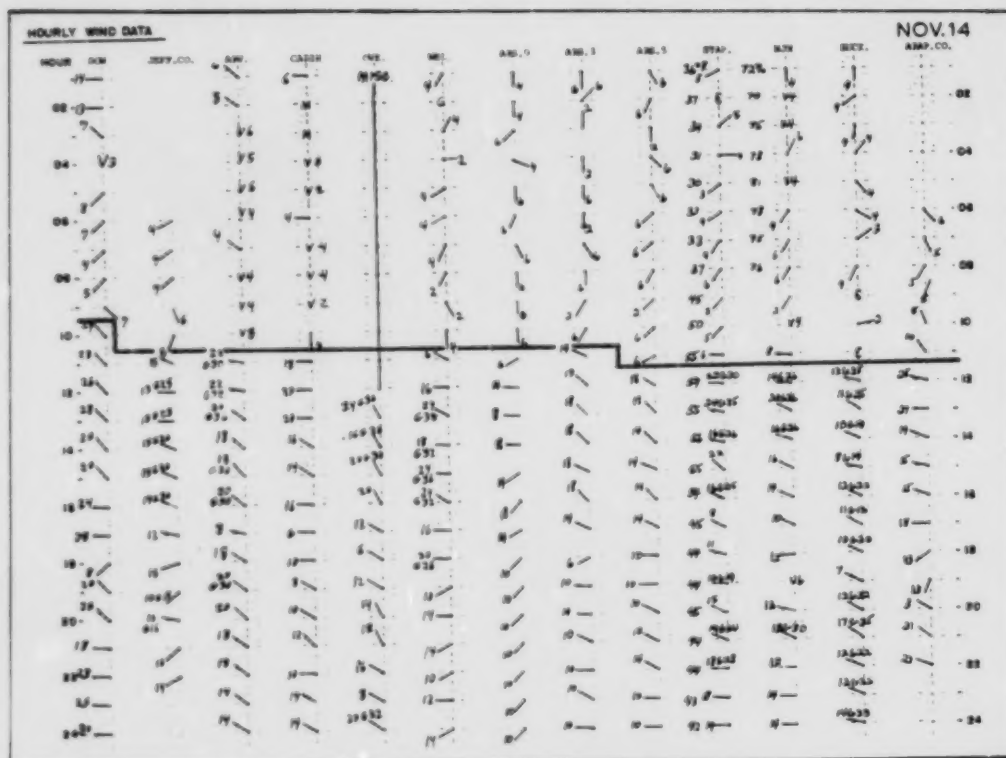


Fig. 11. Hourly sequence of surface wind measurements for November 14, 1973.

for six stations, most of which were in the western portion of the city. The abrupt change for the five wind measuring stations in the eastern portion of the metropolitan area took place between 1100 and 1200. The wind is plotted as follows at each station. The direction indicator ends at a center point for each hourly plotted value. The number at the outer end of the direction indicator shows the wind speed. For instance, a wind from the east at 10 mph is shown as $\text{---}10$. A wind from the northwest at 15 mph is shown as 15--- . "C" stands for calm. "G" followed by a number indicates that the peak gusts in the previous hour reached the level indicated.

Hourly temperatures in $^{\circ}\text{F}$. at Stapleton Airport are plotted to the left of the Stapleton winds. Relative humidity, if above 70 percent, is plotted to the right of the Stapleton winds.

All the hours from noon through midnight on November 14 show a nearly constant flow path over the metropolitan area while strong winds prevailed. This is a good illustration of across-town ventilation.

Episode Days November 16-17

The pollution episode for November 16-17 was primarily concentrated on Friday, the 16th. The airflow patterns on the 16th showed a reversal from downslope to upslope occurring midforenoon and a gradual thinning of pollution density during afternoon hours as the temperature inversion was eliminated.

The set of three photographs in Fig. 12 gives a brief visual sequence of changes in dimension and location of pollution on that day. The photographs at the top and bottom of Fig. 12 show the scene to the northwest from the roof of a tall building in southeast central Denver. At 0840 the upper edge of the visible pollution layer is not yet as high as the tops of the taller buildings in downtown Denver. Note that there is more pollution at the right edge of the 0840 photograph than at the left edge. By 1305 the depth of the polluted air is much greater but the density is less.

The center photograph in Fig. 12 was made at the EPA Trailer toward the west at 1015. An elevated plume of more dense particulate material can be identified just above the trees in the near foreground. The temperature at Stapleton Airport was still only 40° at 1000 and the top of the stable layer was at least 300 meters above the ground. Forced vertical mixing would have been limited to somewhat less than 200 meters at that time.

The hourly sequence of winds at 13 stations is shown in Fig. 13 for the two-day period of November 16 and 17. The beginning of airflow from north to south starts first on the 16th at the lowest elevation stations near the north end of the metropolitan area. The flow of air in the early forenoon hours of the 16th moves the air from over the metropolitan area toward the nearest mountains to the west. During late afternoon of the 16th the airflow gradually changes from northeasterly to southeasterly for most stations on the right shoulder of the Platte River Valley. The airflow shifts around to a westerly component on the left shoulder of the valley near 1700 and 1800. Both the morning and evening changes of wind direction take place during periods of low wind speeds. The nighttime drainage period between the 16th and 17th extended from near 1800 on the 16th through 1000 on the 17th.

The surface temperature inversion was eliminated before 1100 on November 17. (See Fig. 3.) There was a three-hour period of synoptic linkage during the afternoon of November 17 across the entire area. Synoptic linkage occurs when the pressure pattern airflow identifiable on synoptic weather maps is sufficiently strong to override all local terrain control features. This midafternoon period of strong winds ventilated the entire metropolitan area moving air away from the city toward the east on the 17th.

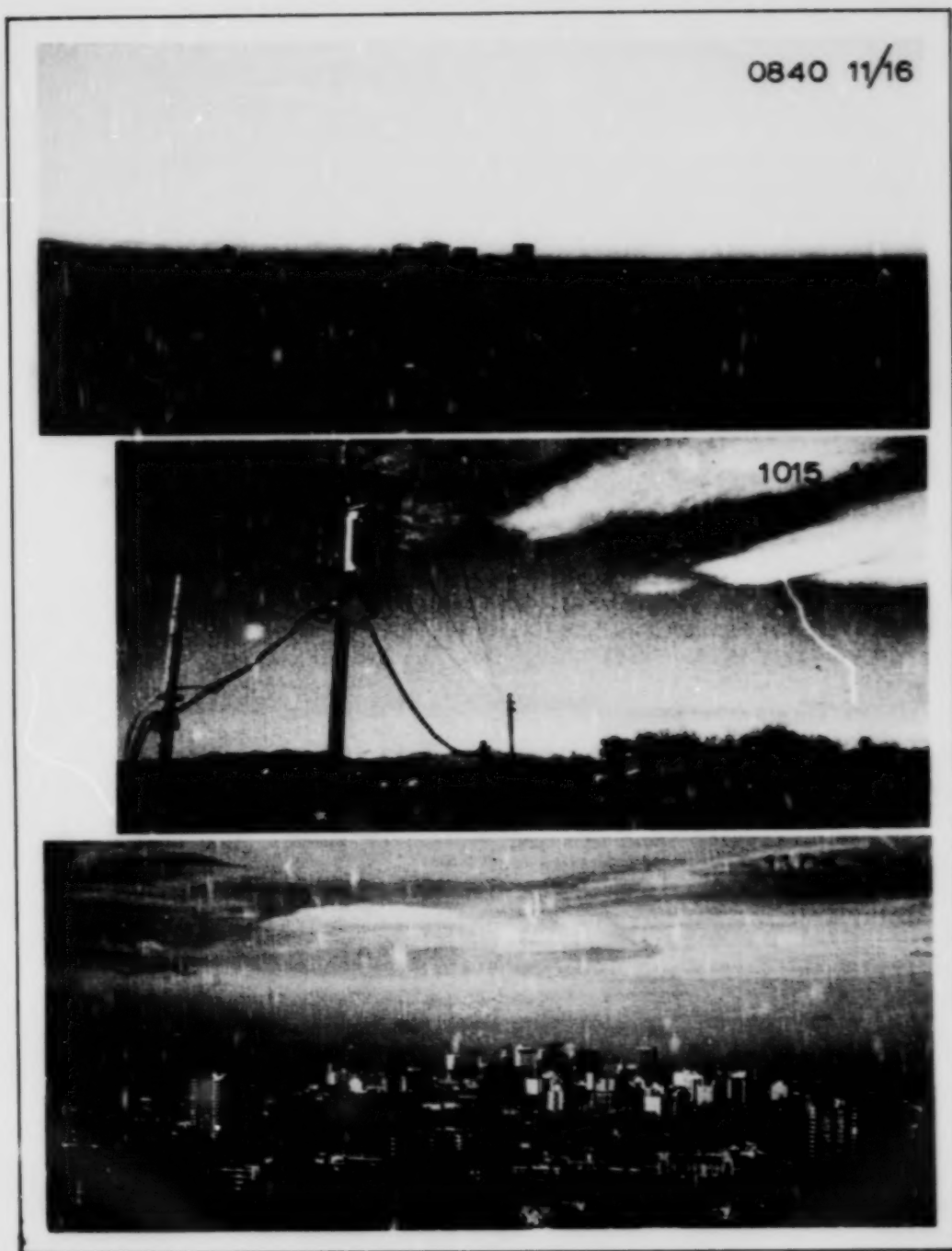


Fig. 12. Photographic record (top and bottom) of contrast from early dense pollution layer and disappearance toward west near noon. Middle photograph shows elevated plume in stable air west of EPA Trailer at 1015, November 16, 1973.

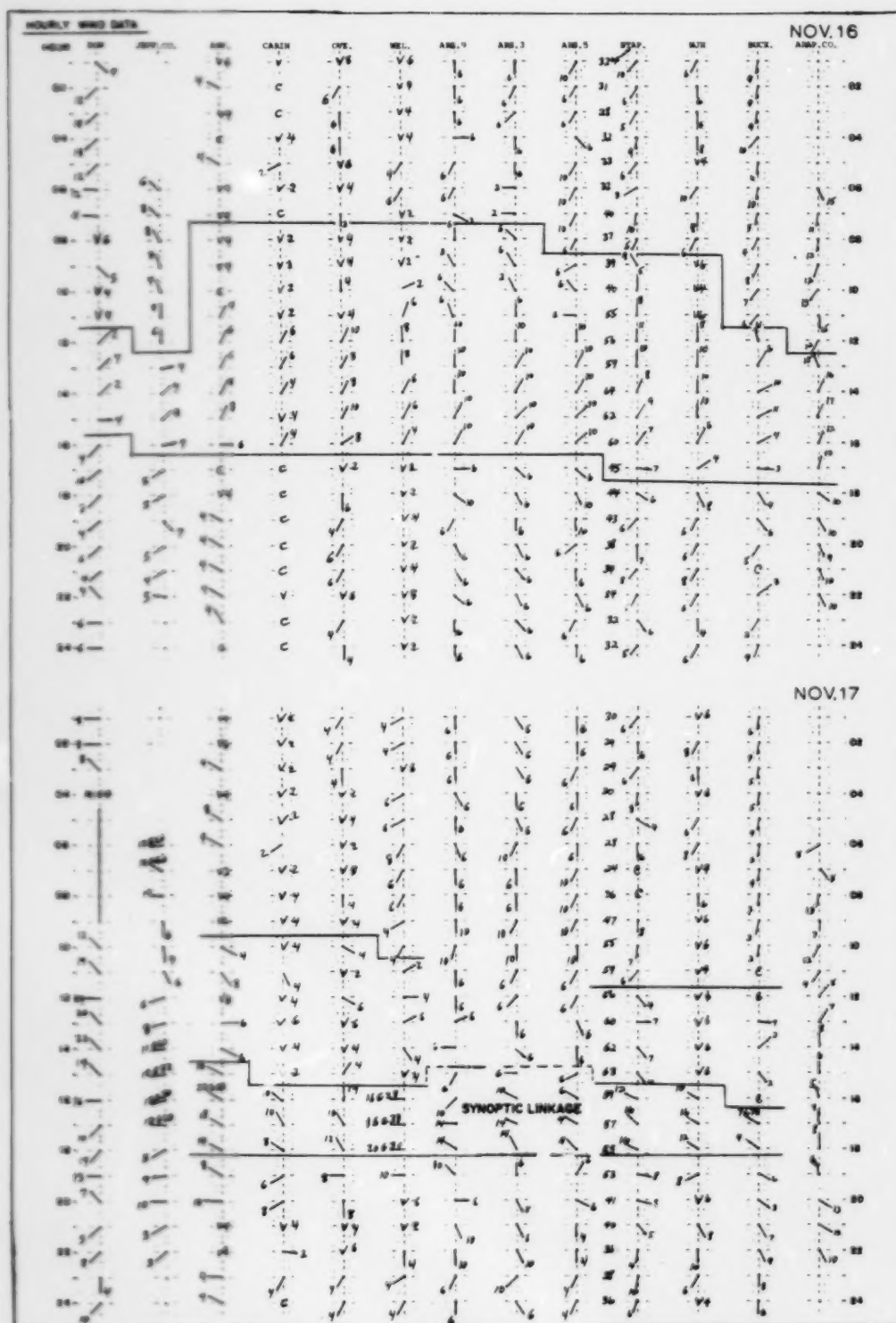


Fig. 13. Hourly sequence of surface wind measurements for Nov. 16-17, 1973.

Episode Day November 21, 1973

November 21 was the second day of a two-day air pollution episode period following a nighttime snowstorm on November 19-20. Airflow after 0800 of the 20th remained from a southerly direction across the metropolitan area. The flow continued to move downslope to the north-northeast from the metropolitan area throughout the night of the 20th. On the morning of the 21st light wind speeds prevailed throughout most of the metropolitan area. Stronger winds were recorded only at Rocky Flats and Jefferson County Airport. The central portion of the city showed a dense layer of pollution in the early forenoon hours. However, this dense layer of pollution was moved horizontally toward the west with the onset of stronger easterly winds beginning between 1100 and 1200 in the eastern part of the city and sweeping across the city by 1400. Figs. 14, 15, and 16 all confirm this type of air motion.

The upper two scenes of Fig. 14 were taken toward the west from the Sheraton Inn-Denver Airport. The first scene at 1100 shows a dense layer of pollution and very little of the skyline of higher buildings in the central part of the city. The second photograph in this figure clearly shows the downtown buildings as being visible and the foreground essentially clear at 1200.

The lower portion of Fig. 14 shows a scene from the roof of a high building in southeast central Denver looking toward the northwest. This photograph was made at 1240. There is much more dense pollution in the left edge of the photograph as compared to the right edge where pollution is being eliminated by stronger winds moving from the east.

Three sequential scenes of pollution to the west of the EPA Trailer between 1125 and 1405 on November 21 are shown in Fig. 15. The scene at 1125 shows a diffuse layer of visible pollution across the Platte River Valley at both edges of the photograph. By 1215, the middle scene, the foreground is much clearer than at 1125. By 1405 the mountain profile directly west of the EPA Trailer is quite distinct and the path of view is quite clean compared with the more dense pollution identifiable at the left edge of the photograph. Soon after the onset of the stronger winds from the east a deck of stratus clouds moved over the metropolitan area. This cloud layer is very noticeable in the lower photograph of Fig. 15.

The sequential pattern of hourly winds on the 21st is portrayed in Fig. 16. When the direction was highly variable a small "v" was used as an indicator. Note that in the nighttime period from 0100 through 0800 there are several stations without distinct indications of direction. Airflow from a northerly component beginning near 0600 and continuing through 0800 at several stations indicates inflow from the northern portion of the city to feed the chimney effect of a rising layer of pollution over the heat island in the central part of the city. The abrupt change in wind speed and the nearly constant direction from

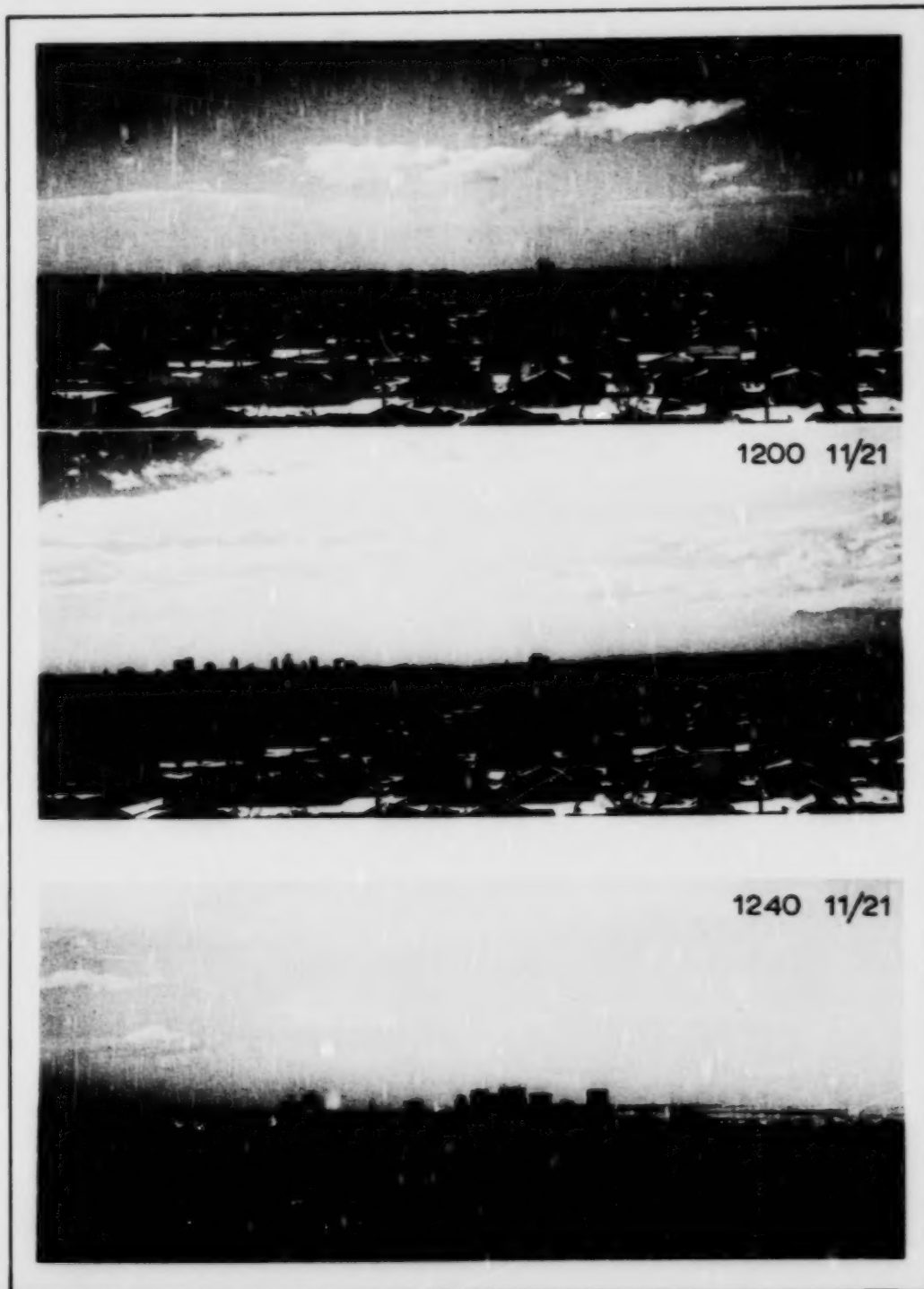


Fig. 14. Set of upper two photographs taken one hour apart from Sheraton Inn toward west-southwest, plus single photograph to northwest from central southeast point which shows progress of polluted layer from east toward west, November 21, 1973.



Fig. 15. Sequential photographs looking west from EPA Trailer from 1125 through 1405, November 21, 1973.

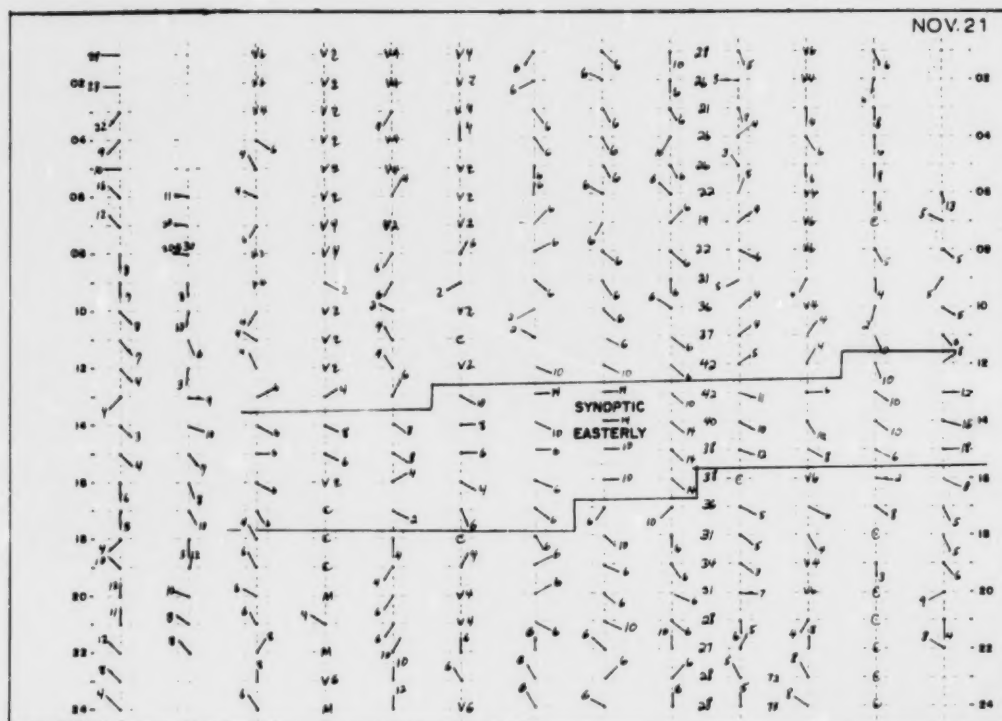


Fig. 16. Hourly sequence of surface wind measurements for November 21, 1973.

an easterly component is easily traced between 1200 and 1400 as the different wind measuring units show the changes in both wind direction and speed. On this day the synoptic flow from an easterly component ventilated the central part of the city and moved the polluted layer toward the southwest corner of the metropolitan area where it continued to be visible through mid-afternoon hours.

SUMMARY

During pollution episode days in Denver, Colorado, it is typical that airflow nearly reverses from downslope to upslope during late forenoon hours. A return to drainage flow takes place gradually in the early evening hours. These multiple changes in general airflow eliminate any possible use of a Steady State Flow concept for dense pollution days.

Depth of the visible polluted layer is directly related to surface heating during daylight hours. The top of the polluted layer matches the upper end of a dry adiabatic lapse rate line as it progresses upward along the morning temperature inversion profile with warmer surface temperatures.

During early afternoon hours there is frequently a detectable air motion carrying polluted air from over Denver toward the west and/or southwest. This air moving toward the mountains replaces air which has already been vertically mixed upward along the relatively warmer mountain slopes. The inversion is broken first over the higher terrain where less solar heating is required to eliminate the more shallow early morning temperature inversions.

There is good evidence that during forenoon hours "Heat Island" effects are often observed to produce an elevated plume moving beyond the downtown area toward the north-northeast. This "Heat Island Plume" continues until surface heating eliminates the coldest layer near the ground.

There is some evidence that a "chimney effect" is produced near the north end of the "Heat Island" in the hours from 0600 through 1000. This "chimney effect" can help draw air from north to south near the surface in the lower part of the valley a few miles north-northeast of the downtown area.

ACKNOWLEDGEMENTS

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Many cooperating agencies and interested persons collected data on an intermittent basis during November, 1973. Only a limited number of individuals who were particularly helpful in collecting meteorological data are listed here.

Personnel from the Colorado Department of Health, Air Pollution Control Division, who very willingly worked on weekend days included Arthur Adams, Charles Bray, Richard Fox, William Retallack, L. Todd Reynolds, Norman Weigel and David Wickham.

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Aerial photographic missions were conducted by photographer Charles Grover.

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Many surface photographs were taken by Fred Crawford of Dow Chemical Company at Rocky Flats and David Netherby of the Sheraton Inn-Denver Airport.

The author acknowledges with thanks the willing cooperation of many other persons and companies who collected wind and temperature data from various locations throughout the Denver metropolitan area.

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THE ANALYSIS OF AMBIENT DENVER AIR FOR ORGANIC VAPORS
INCLUDING CARCINOGENIC POM COMPOUNDS

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ABSTRACT

This paper describes the collection of atmospheric vapors using a chromatographic adsorbent and the subsequent analysis of the sample by gas chromatographic-mass spectrometry. Samples were collected from different locations in the city of Denver, Colorado; comparisons with other urban atmospheres were made where appropriate.

Initial studies concerned a general survey of the nature of compounds found in the ambient Denver atmosphere. Many pollutants most probably arise as a consequence of fossil fuel combustion, but others appear to be a consequence of specific industrial operations. The former compounds are found in every other location studied.

The second phase of this study involved the analysis for polynuclear organic materials in Denver air, particular emphasis being given to the search for carcinogenic species. Comparison is made with ambient Columbus air at a location near an asphalt roofing operation.

INTRODUCTION

The analysis of organic vapors in urban atmospheres has attracted surprisingly little attention, in contrast to the steadily increasing data pertaining to organic particulates. However, a number of collection and analysis techniques have been reported recently. Several cryogenic sampling methods have been reported, but this method invariably lacks sensitivity due to the poor sample concentration which may be obtained because of the presence of large quantities of water and low-

molecular weight hydrocarbons present in the atmosphere¹⁻⁹.

The more efficient methods described for the collection all involve solid absorbents, principally: activated charcoal¹⁰, carbosieve¹¹, Poropak Q¹², Chromosorb 102^{13,14}, Tenax GC¹¹. Charcoal and Carbosieve are the least satisfactory for high sensitivity sample collection, since both retain appreciable quantities of water; furthermore, charcoal has a very low sampling capacity, while both are difficult to desorb unless solvents are employed. Desorption with solvents precludes high sensitivity because of sample dilution and the risk of contamination. Chromosorb and Tenax GC appear to be the most promising adsorbents which have been used to date. Dravnieks¹³ and Crittenden¹⁴ have described efficient collection systems using Chromosorb 102, the former carrying out analysis by gas chromatography following hot desorption of the sample into a low-temperature syringe needle and the latter attempting direct high resolution mass spectrometric analysis of the desorbing sample. In both cases it appears that relatively small volumes of air were sampled and high sensitivity was not sought. Crittenden collected both particulates and vapor simultaneously, and while the high resolution mass spectrometric analysis of particulates is particularly elegant, no evidence is presented which would suggest that this is an effective means for analysis of organic vapors. There is no doubt that Tenax GC is also an efficient absorbent, as demonstrated by Zlatkis for a variety of systems. The high-temperature limit of Tenax may prove more useful than Chromosorb in some systems. The sampling of large volumes of air has not been attempted with Tenax, but it should be comparable to Chromosorb. In this program, Chromosorb 102 has been employed as adsorbent, and up to 30,000 liters of air has been routinely sampled as described in the following section.

The present study is primarily concerned with the determination of compounds with six or more carbon atoms; it is particularly directed towards the detection of oxidized hydrocarbon species and the detection of hazardous polycyclic organic materials (POM). The principal urban location studied was Denver, Colorado. Limited analyses were also carried out on vapor samples collected at St. Louis, Missouri, and Columbus, Ohio, for comparison with the former data. Lastly, a simple diurnal study of pollutant concentrations was made in Columbus, Ohio, in an attempt to estimate their possible origin. Some evidence for ambient photo-oxidation of gasoline-type hydrocarbons was obtained in this experiment.

EXPERIMENTAL

Preliminary experiments were carried out with Chromosorb 102 chromatographic columns in which retention time data for typical anticipated pollutants were obtained at various temperatures. Optimum dimensions were then calculated for ambient atmospheric sampling columns (15 cm long, 1.5 cm radius), and several were fabricated and packed with approximately 35 g of Chromosorb (Figure 1). The sampling columns were

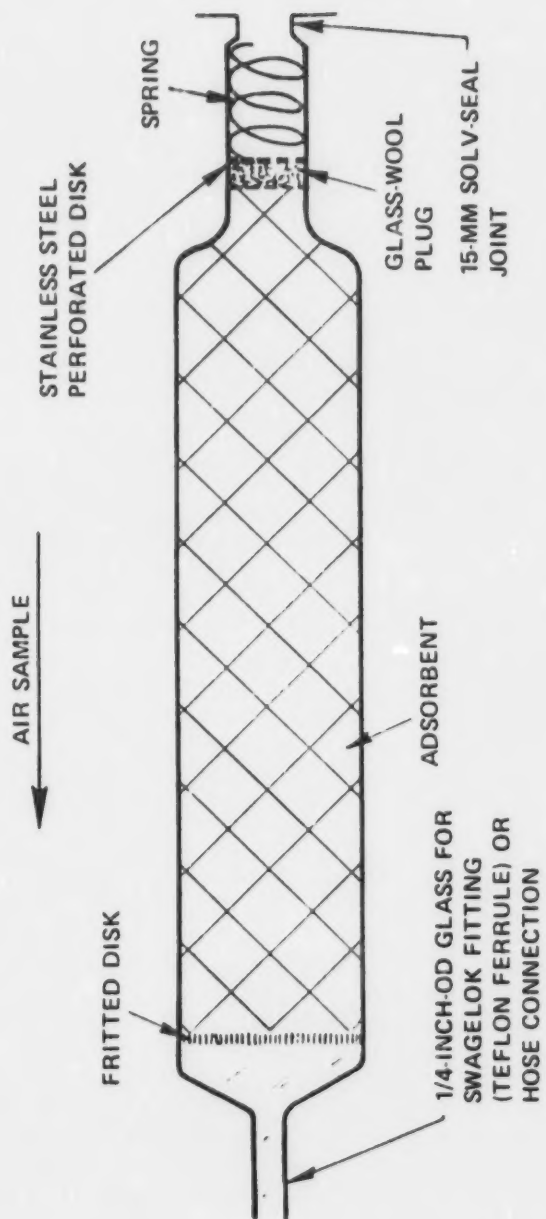


Figure 1 ATMOSPHERIC SAMPLING COLUMN

initially conditioned at 200 C with a nitrogen flow rate of 500 ml min⁻¹ for 48 hours.

The design of the sampling columns permits the incorporation of a filter holder at the entrance of the column, by means of a 15 mm glass and Teflon "Solv-Seal" joint. A 4-inch glass fiber filter was routinely employed. Filtered ambient air may be drawn through the sampling columns at approximately 12 liter min⁻¹ by means of a Gast 0522 rotary vacuum pump. In this study the filter was discarded.

Prior to sample desorption, traces of water (and some lower molecular weight hydrocarbons) were removed from the sampling columns by purging with prepurified dry helium (liquid-nitrogen trap in series with an activated 3A molecular sieve column), in the same direction as the original sampling procedure, for 30 minutes at 2 liter min⁻¹. During this procedure several internal standards were added during some experiments in order to facilitate the computerized gas chromatographic-mass spectrometric quantification of POM compounds, as described later. Desorption of the collected sample is achieved by heating the sampling column in an oven to 170 C and back-flushing the column with prepurified helium (liquid-nitrogen trap) for 30 minutes into a 12 cm x 1 mm stainless steel loop cooled with liquid nitrogen. Repeated desorptions demonstrated the sufficiency of this time period. The desorption/chromatograph injection valve connections are shown schematically in Figure 2. Injection of the sample onto the gas chromatographic column is achieved by firstly directing the carrier gas through the cold stainless steel loop and then flash-heating the loop to 250 C when the sample is immediately swept onto the head of the gas chromatographic column. When methane carrier gas is used for chemical ionization mass spectrometry, the cooled stainless steel loop is initially warmed to -80 C (isopropanol-solid carbon dioxide) prior to diverting the carrier gas through it.

The gas chromatographic columns routinely used in this program were an 8 m x 2 mm 3 percent Silar 5CP column, programmed at 2 C min⁻¹ from 60 C to 180 C, and 3 m x 2 mm 3 percent Dexil 300, programmed at 4 C min⁻¹ from 170 C to 350 C, in a Finnigan gas chromatograph. Gas chromatographic-mass spectrometric analysis is readily achieved since the chromatograph is interfaced with a Finnigan 1015 quadrupole mass spectrometer (equipped with a chemical ionization source) through appropriate heated stainless steel capillary tubing and sampling valve. The characteristics of this mass spectrometer do not require any molecular separator at the interface. The mass spectrometer is controlled by a System Industries 150 data acquisition system and Digital PDP8 computer equipped with a very wide variety of programs for manipulation and display of data.

RESULTS AND DISCUSSION

Preliminary experiments were carried out in order to establish optimum sampling column desorption times at 170 C, with a helium flow

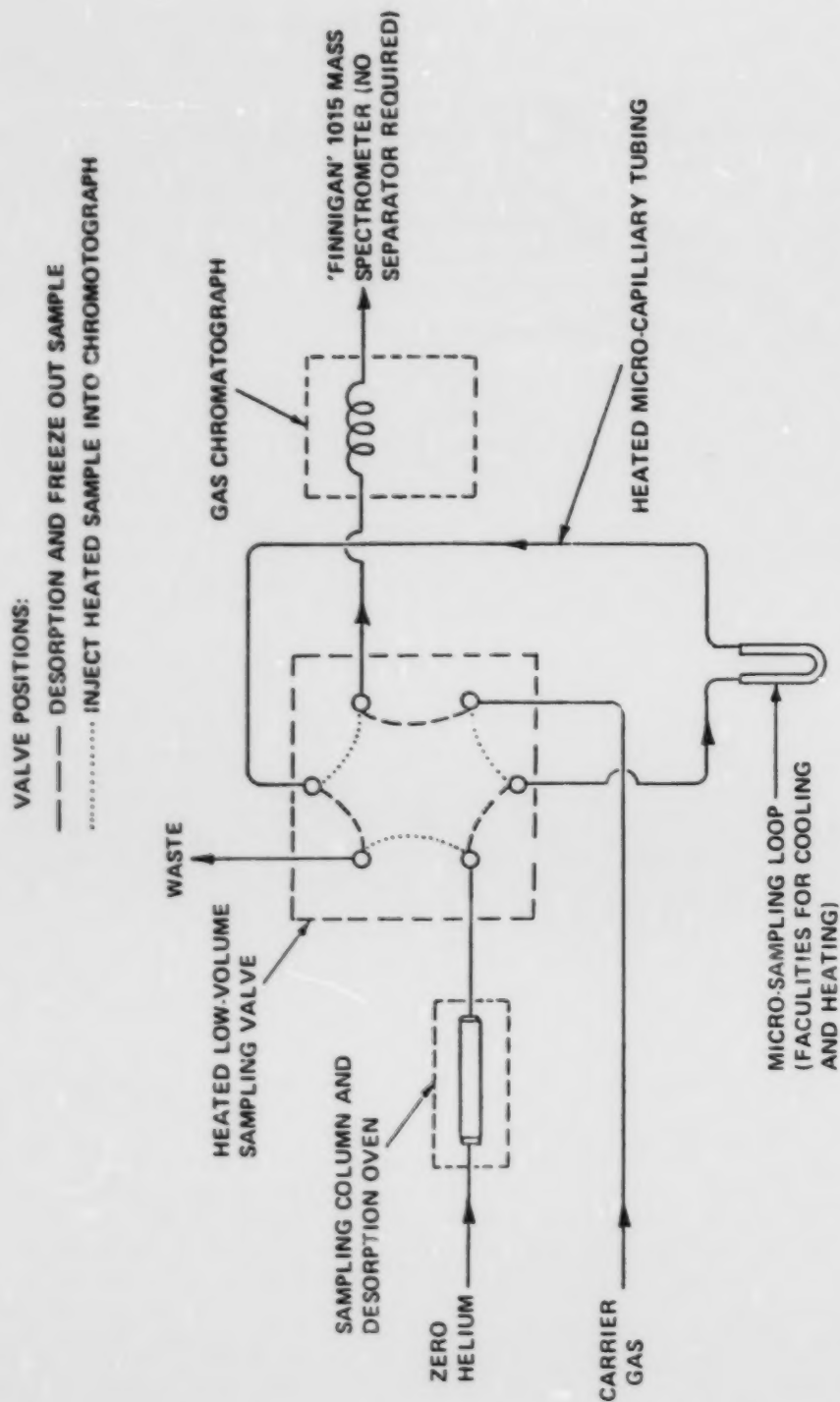


Figure 2 DESORPTION OF SAMPLING COLUMN AND INJECTION OF SAMPLE INTO GAS CHROMATOGRAPH - MASS SPECTROMETER

rate of 500 ml min^{-1} . Furthermore, by using the columns in series it was established that the compounds of interest did not break through one column under normal operating conditions. It was found desirable to remove water from the sampling columns prior to sample desorption (see earlier) to avoid plugging the cooled desorption loop with ice; it was established that the helium purge used for this purpose did not affect the integrity of the collected sample. By means of duplicate sampling and chromatographic analyses, it was established that sealed samples could be refrigerated for at least 10 weeks without apparent change.

Survey Analysis of Vapor Contaminants

Duplicate atmospheric collections of approximately 17,000 liters were made in Adams City (Denver, Colorado), St. Louis, Missouri, and Columbus, Ohio. The Denver sample was collected towards the end of a temperature inversion episode on December 12-13, 1973. The St. Louis and Columbus samples were both collected towards the end of November, 1973; intermittent rain and overcast skies were encountered at St. Louis while clear skies persisted during the Columbus sampling period. All of the samples were subject to gas chromatographic-mass spectrometric analysis (Silar 5CP column) using chemical ionization with methane (CI), and the compounds identified are listed in Table 1. A typical reconstructed gas chromatogram is shown in Figure 3, the major peaks identified are indicated on the figure. Identification was based upon mass spectra and relative chromatographic retention times, but specific isomer assignment was not always possible. Many of these compounds appear to be representative of partially burnt fuel from internal combustion engines; it is possible that the naphthalene derivatives are formed by combustion of lower molecular-weight hydrocarbons in the manner proposed by Badger¹⁶. Tolualdehydes and phthalaldehydes are presumably formed by partial oxidation of xylenes, either photochemically or in combustion processes. However, some compounds such as methyl methacrylate, chlorobenzene, bipyridyl, dimethyl styrene, benzonitrile, and pyridine, would appear to have originated from a local industry since it is difficult to envisage other reasons for their presence.

Diurnal Variation Studies

In order to attempt to demonstrate the possible origin of ambient atmospheric pollutants, a simple diurnal variation study was carried out in Columbus, Ohio. Seven sampling intervals were selected during a 24-hour period, the Chromosorb 102 sampling columns were subsequently desorbed and analyzed for fourteen previously detected compounds which were well resolved by gas chromatography (Silar 5CP column). The results were quantified by calibration of the chromatograph with standard solutions of the compounds of interest at concentrations of 200 ng per μl in methylene chloride or acetone, and are shown in Table 2.

Table 1. OCCURRENCE OF VOLATILE COMPOUNDS
IN DIFFERENT URBAN ATMOSPHERES

Compound	Location*		
	Denver (Adams City)	Columbus	St. Louis
Hexene	X	X	X
Heptene	X	X	X
Toluene	X	X	X
Xylenes	X	X	X
Trimethyl benzenes	X	X	X
Tolualdehydes	X	X	X
Naphthalene	X	X	X
1-Methyl-naphthalene	X	X	X
2-Methyl-naphthalene	X	X	X
Dimethyl-cumene	X	X	
Phthalaldehydes	X	X	
Phenol	X	X	
Methyl methacrylate	X		X
Allyl phenol	X		X
Chlorobenzene	X		
Tetrahydronaphthalene	X		
2,3-Dihydro-methyl-benzofuran	X		
Methyl-allyl-phenol	X		
Bipyridyl	X		
Dimethyl-styrene	X		
Tetrahydro-methyl-naphthalene	X		
Benzonitrile		X	
Propiophenone		X	
Dimethyl-naphthalene		X	
Methyl-benzyl alcohol		X	
Hydroxy-biphenyl		X	
Amino-methyl-acetophenone		X	
Tetramethyl benzene			X
Pyridine			X
Benzoquinone			X
Benzophthalaldehydes			X

* X indicates >0.01 ppb detected.

FIGURE 3. GC-MS(CH₄) OF AMBIENT DENVER AIR (DECEMBER 12-13, 1973)

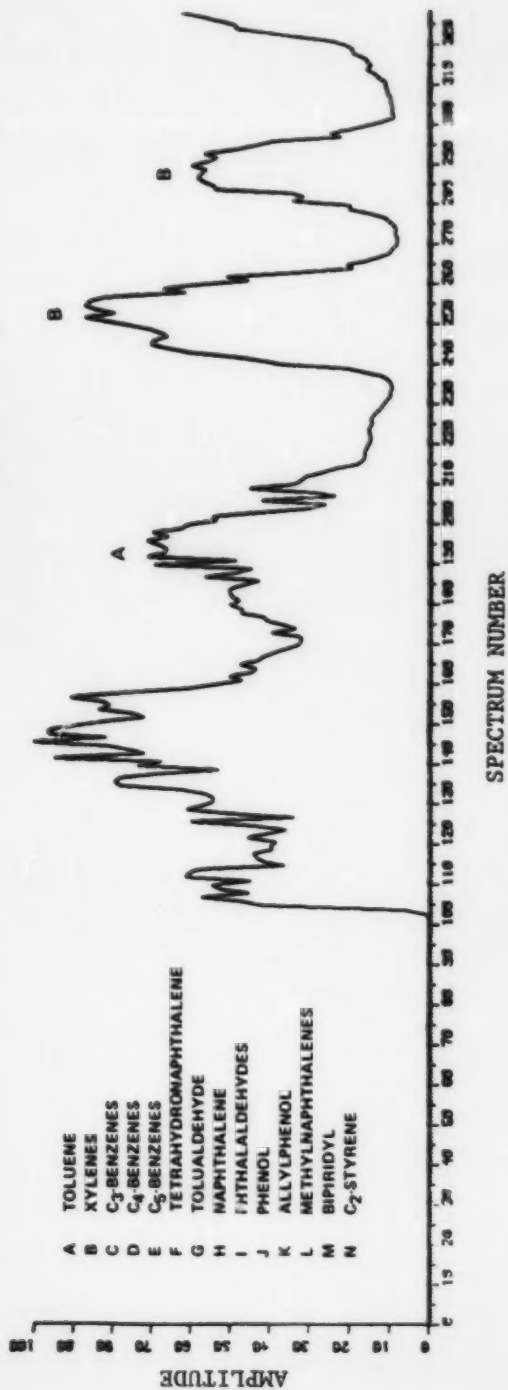


FIGURE 3. GC-MS(CH₄) OF AMBIENT DENVER AIR (DECEMBER 12-13, 1973) (Continued)

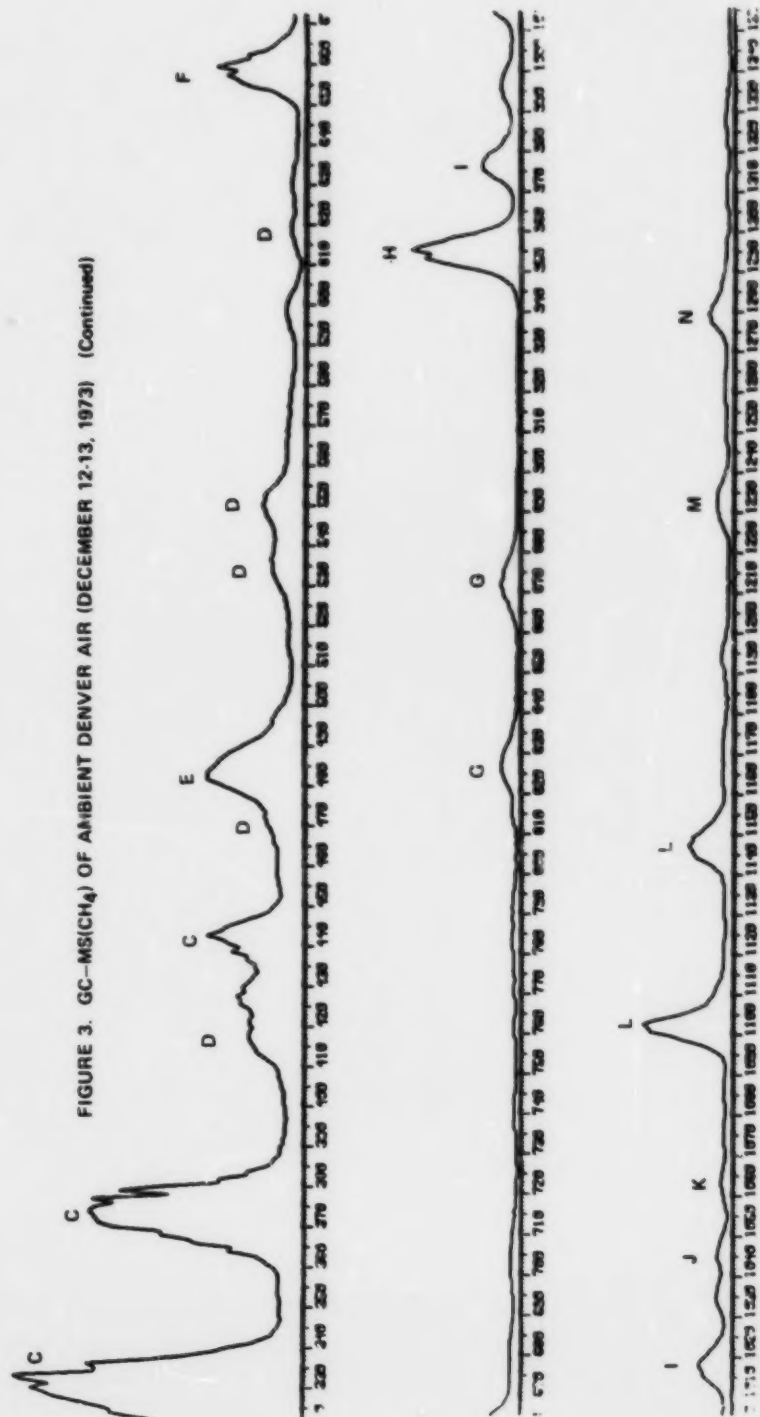


Table 2. AVERAGE POLLUTANT CONCENTRATIONS (ppb) IN AMBIENT COLUMBUS AIR

(22-23 February, 1974)

45 to 50 F, clear skies until 9:00 p.m., heavy rain 10:00 p.m. onwards

	6:30 to 9:00 am	9:00 to 11:30 am	11:30 to 2:00 pm	2:00 to 4:30 pm	4:30 to 7:00 pm	7:00 to 10:15 pm	10:15 to 6:30 am
Toluene	0.86	0.47	0.50	0.48	0.36	0.32	0.17
Xylenes	0.80	0.32	0.47	0.33	0.27	0.21	0.10
Trimethylbenzenes	0.26	0.17	0.24	0.16	0.11	0.08	0.04
Cumene	0.32	0.14	0.15	0.16	0.17	0.16	0.04
Naphthalene	0.25	0.14	0.20	0.21	0.22	0.19	0.03
1-Methyl naphthalene	0.20	0.08	0.07	0.06	0.04	0.03	0.02
m-Tolualdehyde	0.01	0.04	0.03	0.03	0.02	0.004	0.001
p-Tolualdehyde	0.04	0.14	0.17	0.21	0.11	0.10	0.02
o-Phthalaldehyde	0.000	0.000	0.005	0.04	0.07	0.03	0.01
p-Phthalaldehyde	0.000	0.000	0.000	0.001	0.002	0.001	0.000
Propiophenone	0.07	0.09	0.11	0.13	0.13	0.12	0.03
Benzonitrile	0.04	0.03	0.06	0.05	0.05	0.19	0.02
Phenol	0.04	0.03	0.04	0.045	0.025	0.03	0.000
Phthalic anhydride	0.000	0.000	0.000	0.005	0.01	0.009	0.000

The low ambient concentrations during the final sampling period are presumably due to the heavy and continuous rain which began during this time. All of the hydrocarbons exhibit maximum concentrations during the early daylight hours, and all except 1-methyl naphthalene show a lesser peak later in the day. The variations in the concentrations of the alkyl benzenes may be related to the density of automobile traffic, although if this is the case it is surprising not to see a peak in the early evening. The concentrations of the naphthalenes are higher than might be expected, in view of their lower volatility than the other hydrocarbons; this high concentration may be caused by a large nearby stationary source, such as fossil-fuel heating unit.

The concentration profiles for the four aldehydes analyzed suggests that the tolualdehydes and phthalaldehydes are formed by sequential oxidative degradation of the corresponding xylenes. Within the limitation of the number of measurements made, the tolualdehydes appear to peak shortly after noon, while the more highly oxidized phthalaldehydes peak in the late afternoon. This would appear to be consistent with stepwise photo-oxidation of xylenes. The concentration profile for phthalic anhydride appears to be parallel to those of the phthalaldehydes, but the reason for this remains obscure.

The concentration of propiophenone, benzonitrile, and phenol appear to be independent of both time and the fluctuations of other compounds measured, which would suggest that such compounds may originate from relatively constant stationary sources such as manufacturing industries.

Analysis for Potentially Carcinogenic Polynuclear Aromatic Compounds

The earlier described survey analyses indicated the abundance of naphthalenes in the ambient atmospheres studied, and thus a detailed study of polynuclear aromatic compounds in Denver air was made using an identical collection technique.

The saturated vapor pressure for commonly occurring POM under ambient conditions is estimated to be approximately 50 ppb, based upon the only available data, which has been obtained for anthracene. The concentrations of specific POM's found in ambient atmospheres are expected to be several orders of magnitude lower than this, thus, the probability of these species being present in the vapor phase is high. While some POM compounds may be adsorbed on the surface of particulate matter to varying degrees, even this may be partially or wholly reentrained as vapor following filtration, impaction, or precipitation of particulate matter in a sampling train. Thus, it is essential to ensure that volatile POM vapors may be efficiently collected since the majority of these species will be collected in this state. Our previous work in this area has demonstrated that the majority of ambient POM material may only be effectively collected as vapor.

Samples for POM analysis were collected at two locations in Denver (Table 3) and also at a Columbus location in close proximity to an asphalt roofing operation. While the latter sample is of course atypical of urban ambient air as a whole, the results clearly demonstrate that such operations are significant contributors to ambient POM (Table 3).

Quantitative analysis for POM species was carried out by GC-MS analysis of the desorbed vapor samples. Prior to desorption, appropriate quantities of 9-methylanthracene, 9-phenylanthracene, and 9,10-diphenylanthracene were injected into the samplers during water vapor removal, to serve as internal standards for identification and quantification purposes. Identification of the POM species present was made on the basis of their mass spectra, and retention time relative to the internal standards. Quantification was made upon the basis of specific absolute ion current integration, with reference to the quantities of internal standards present. We have previously demonstrated that this quantification procedure has a reproducibility of better than 7 percent^{17,18}. In an ongoing modification of the computer program, the entire procedure is being automated, with the aid of data bases of mass spectra, retention times relative to the internal standards, and response factors relative to the internal standards¹⁸. The quantitative analyses for POM compounds from each location studied are shown in Table 3, the possible error in these values should not exceed 20 percent.

Reconstructed gas chromatograms are shown in Figures 4A and 4B, which show reconstructed gas chromatograms for both ambient Denver air samples. The peaks identified are shown in the respective figures. The chemical ionization (methane) mass spectra of POM compounds are simple and characteristic; the base peak is always the protonated molecular ion ($M + 1$) and adduct ions are usually seen at ($M + 29$) and ($M + 41$), due to addition of C_2H_5 and C_3H_5 species in the mass spectrometer. Fragmentation is not usually observed.

It is not surprising that by far the highest concentration of POM species was found in the vicinity of the asphalt roofing operation (Table 3), but it is also interesting to note that significant quantities of these species were present in the ambient Denver samples.

The suburban and industrial locations monitored in Denver exhibit relatively small differences, although the total POM loading is almost twice as high at the industrial location. The total loading of known carcinogenic POM (Benz(c)phenanthrene, benz(a)anthracene, methylchrysenes, benzpyrenes, and methylcholanthrenes (--as rated by the National Academy of Sciences) is almost four times higher in the industrial area, which may be partly explained by the presence of an asphalt blowing operation half a mile upwind of the sampling site. However, the benzpyrenes alone are significantly higher at the suburban location. These limited POM data clearly indicate the importance of vapor phase POM compounds, since several of these materials are known carcinogens. Further data at a wide variety of sites are evidently required in order to establish truly significant comparisons.

Table 3. ANALYSIS OF AMBIENT POM VAPORS
AT DIFFERENT URBAN LOCATIONS

Compound	Concentrations at Each Location, ppb		
	Suburban Denver ¹	Industrial Denver ²	Columbus ³
Anthracene/phenanthrene	0.73	0.37	64
Methylanthracenes	0.49	0.008	51
Fluoranthene	0.086	0.048	4.5
Pyrene	0.09	0.012	7.3
Methyl pyrenes and fluoranthenes	--	0.11	↑ less than 0.1 ppb each ↓
Benz(c)phenanthrene	0.012	0.083	
Chrysene/benz(a)anthracene	0.09	0.46	
Methyl chrysenes and benzanthraces	0.09	0.48	
Benz(k+b)fluoranthenes	0.09	0.025	
Benz(j)fluoranthene	0.022	0.0046	
Benz(a+e)pyrenes	0.083	0.018	
Perylene	--	0.002	
Methylcholanthrene	0.004	0.002	

1 Aurora.

2 Adams City, adjacent to northern perimeter of oil refinery.

3 Adjacent to asphalt roofing operation.

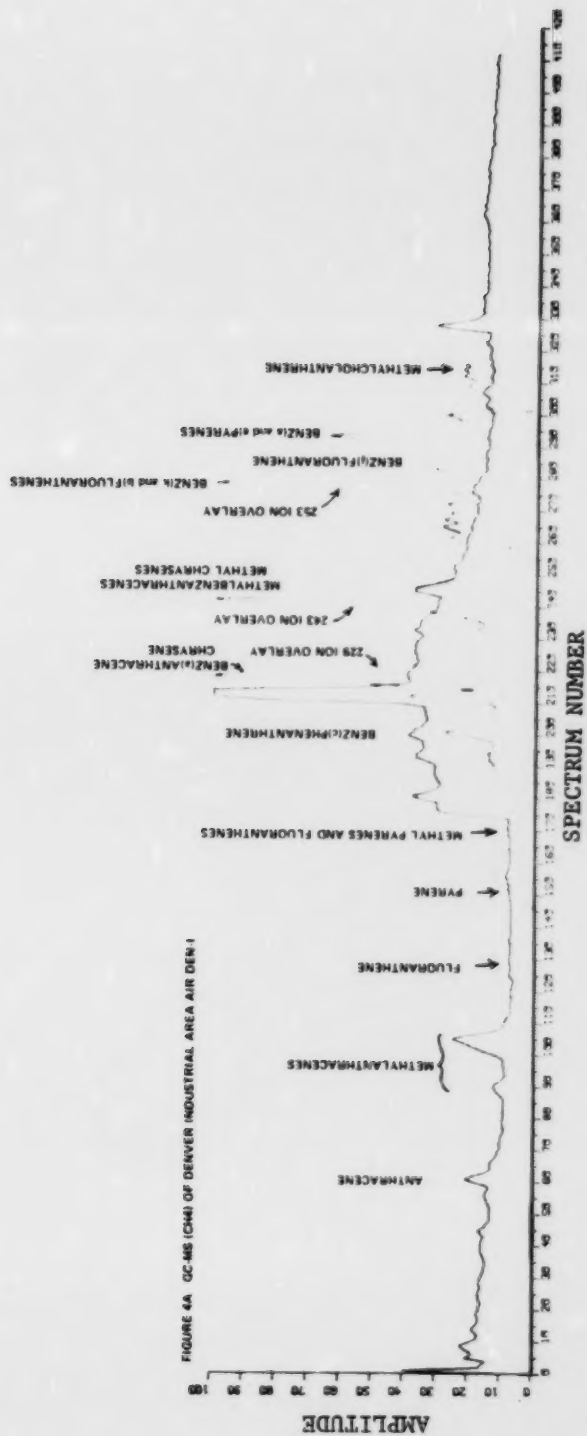
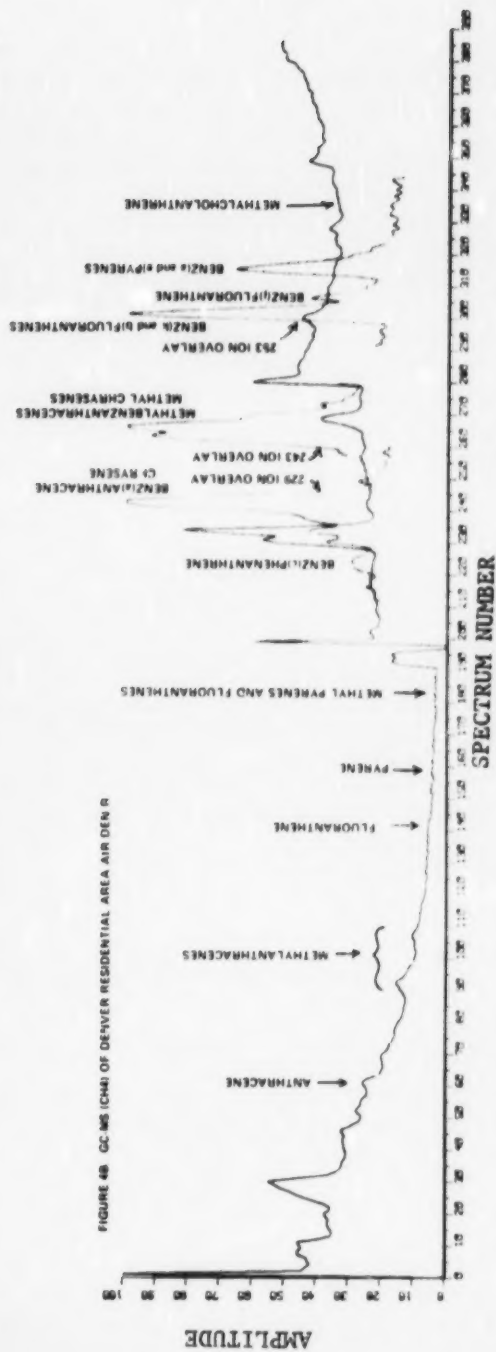


FIGURE 4A GC-MS (CH4) OF DENVER INDUSTRIAL AREA AIR DEN 1



CONCLUSIONS

The results of these studies demonstrate the suitability of the sampling and analytical methods described to problems associated with the analysis of polluted atmospheres. While survey analysis gives an overall picture of an atmosphere, diurnal variation studies may give insight into the origin of pollutants, as well as being an aid to mechanistic studies. These methods are particularly amenable to the detection and quantification of trace quantities of polynuclear aromatic compounds in ambient atmospheres, and highlight the importance of considering the presence of carcinogenic species which are present in the vapor phase.

ACKNOWLEDGEMENTS

We wish to thank Dr. L. Todd Reynolds of the Colorado Department of Health for collecting the ambient air samples in Denver in December, 1973, and March, 1975.

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APPENDIX

In view of the apparent importance attached to the monitoring of POM emissions into the atmosphere, we have recently developed a novel sampling system for high temperature stack emissions of these and other organic species. The Adsorbent Sampler (Figure 5) is based partly upon data from the present study, and has been shown to facilitate quantitative collection and analysis of POM species, in contrast to the less efficient aqueous impinger methods. The Adsorbent Sampler for stack gases have been shown to be between 2.3 and 30 times more efficient than

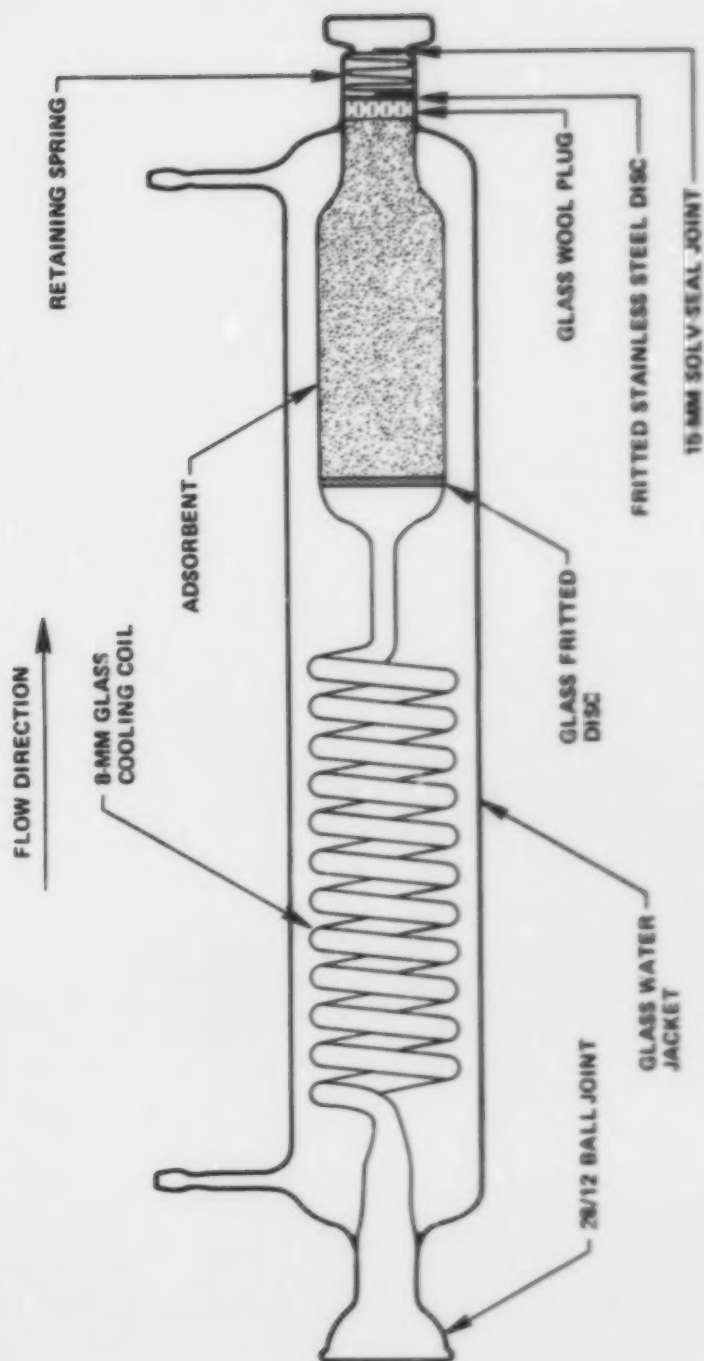


FIGURE 5. ADSORBENT SAMPLING SYSTEM

conventional impinger methods, including EPA Method 5, depending upon the nature of the combustion process. This development was sponsored by the Electric Power Research Institute and the U.S. Environmental Protection Agency.*

NOTE ADDED IN PRESS

In the section entitled "Analysis for Potentially Carcinogenic Polynuclear Aromatic Compounds," it has been brought to our attention that the Industrial Denver Sample (Table 3) was in fact obtained near to asphalt production and asphalt blowing operations. This appears to explain an apparent anomaly in Table 3, in that the concentration of methyl pyrenes, benz (c) phenanthrene, chrysene/benz (a) anthracene, methyl chrysenes, and methyl benzantracenes appear to be abnormally high. We have shown that all of these compounds are relatively abundant in asphalt production in previous studies for the U.S. Environmental Protection Agency.

* Jones, P. W., R. D. Giammar, P. E. Strup, and T. B. Stanford.
Efficient Collection of Polycyclic Organic Compounds From Combustion Effluents. (Presented at 68th Annual Meeting of the Air Pollution Control Association. Boston. 1975.)

LIDAR OBSERVATIONS OF ATMOSPHERIC PARTICULATES NEAR
DENVER, COLORADO

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ABSTRACT

Lidar observations were made by WPL-(NOAA) of the cloud of pollution often observed near the Platte River Valley north of Denver, Colorado, during the EPA sponsored Denver Air Pollution Field Study of November 1973. The lidar was located at the Adams County Fair Grounds, near Henderson, during the period 15-29 November. During this time four days of data were obtained on smog conditions, namely 16, 21, 26, 29 November. This data is reported, analyzed and compared with other observations taken simultaneously. From the lidar, estimates may be made of total aerosol content up to the inversion level, given a ground calibration.

INTRODUCTION

In the fall of 1973 the Wave Propagation Laboratory (WPL) of the National Oceanic and Atmospheric Administration (NOAA), U.S. Department of Commerce, was invited by J. Durham, Environmental Protection Agency, Research Triangle Park, North Carolina, to participate in an observation with EPA and other organizations on the location, concentration and character of pollutants in the atmosphere over and near Denver, Colorado. Personnel of WPL had just then brought into operation a new major lidar system and agreed to join the observation at NOAA's expense.

Essential parts of the lidar system were operational, but the data recording was not yet complete, complicating the processing and analysis. Calibration procedures were not then complete, hence only

relative signals could be measured. In spite of these inflexibilities the lidar could give valuable information on the presence of aerosols in the atmosphere above the ground. It could provide profiles of aerosol backscatter as a function of time for comparison with other observations. Further, it could, aided by auxiliary data and under conditions found generally to occur, allow determination of aerosol concentrations as a function of time and altitude.

It is probably not a law of nature that expected atmospheric events often fail to occur when a considerable effort is made to observe them, but atmospheric scientists will not be surprised to know that during the period 15-30 November 1973, when the lidar was on station, only certain periods during four days occurred in which the lidar and most other observation stations were operating and the meteorological conditions contributed to significant smog formation. It is the record of these four days and the correlation of the lidar soundings with other observations that are the subjects of this report. Data from other days will be used to establish "clear air" or background calibration. During most of the other days smog was light or nonexistent, sometimes arising briefly, to be swept away by clean wind from the west.

OUTLINE OF EXPERIMENT

The persistence of a brown cloud of pollution which has caused a steady degradation of visibility in the area over and surrounding Denver, Colorado has become the object of concern of the Atmospheric Aerosol Research Section, Chemistry and Physics Laboratory, Environmental Protection Agency, National Environmental Research Center of Research Triangle Park, North Carolina. This agency conducted an aerosol characterization program during November 1973 in the Denver area to determine the composition and source of this pollution cloud. This effort involved monitoring by aircraft as well as the use of a number of ground stations.

The investigation was an attempt to determine the importance of photo-chemical reactions, automobile exhaust emissions, industrial emissions and wind-blown soil in the formation of the pollution cloud. The instrumentation used and measurements taken during the experiment are presented in the accompanying Table 1.

In addition to the Atmospheric Aerosol Research Section of the Environmental Protection Agency other participating groups included NOAA, National Center for Atmospheric Research (NCAR), the University of Denver, the University of Washington, General Motors, Thermo-Systems Inc., IIT Research Institute and the Meteorology Research Institute.

The geographic area of greatest concern was a segment of the South Platte River drainage extending from a few miles up-river to a few miles down-river from the center of Denver. The accompanying map,

Table 1. PROPOSED MEASUREMENTS AND THEIR APPLICATIONS

<u>Instrumentation</u>	<u>Type of Analysis</u>							<u>Aerosol Distributions</u>				<u>Source Inference</u>				
	Gravimetric	X-ray Fluorescence	X-ray Diffract.	Atomic Absorption	CHN Analysis	Optical Microscopy	Scan. Elect. Microscopy	Chemical	Mass	Surface	Number	Photochemical	Industrial	Wind-Blown Dust	Other	
<u>Aerosol Samplers:</u>																
Hi-Vol/Andersen	✓			✓	✓	✓	✓		✓	✓						
Lundgren Cascade		✓				✓	✓	✓					✓	✓	✓	
Andersen Cascade	✓								✓	✓						
Total Membrane Filter		✓	✓	✓				✓				✓				
<u>Aerosol Monitors:</u>																
Condensation Nuclei Counter:	May relate to:															
	(a) aerosol formation rate										✓					
	(b) age of aerosol cloud										✓				✓	
Electrical Mobility Analyzer									(✓)	(✓)	✓					
Single Particle Optical Counter									(✓)	(✓)	✓					
Integ. Nephelometer with Rel. Hum. Control								✓								
Lidar									(✓)		(✓)					
<u>Gas Detectors:</u>																
Dew Point									✓				✓	✓		
Total Hydrocarbon									✓				✓	✓		
Methane									✓				✓	✓		
Ozone									✓				✓	✓		
Oxides of Nitrogen									✓				✓	✓		
Carbon Monoxide									✓				✓	✓		
Sulfur Dioxide									✓				✓	✓		
<u>Weather Monitors:</u>																
Wind Speed															✓	
Wind Direction													✓	✓		✓
Temperature Gradient													✓	✓		
Solar Light Intensity													✓			
Ultraviolet Light Intensity													✓			

Fig. 1, identifies the area and shows the location of the data collection points used in the study. The 5200 and 5500 ft contour lines indicate the downward slope of the terrain on both sides of the South Platte River. The drainage basins formed of Sand Creek in the northwest direction from Buckley Air National Guard Base past Stapleton International Airport into the Platte River along with the combined drainage of Clear Creek and Ralston Creek from the west past Golden and Arvada help influence the local windflow patterns in these portions of the metropolitan area. The EPA CAMP* station is located nearly in the center of the area. Pibals were released at the locations shown in Arvada, at the Yellow Cab Company and at the EPA Trailer site. Other observation sites were located at Stapleton, Buckley, Jefferson County (JEFFCO) and Arapahoe County (ARAPCO) Airports, the Federal Center, Rocky Flats, Welby (WEL), Overland Park (OVE), National Jewish Hospital (NJH), Children's Asthmatic Research Institute and Hospital (CARIH), the Denver Trout Farm (TRA) and at Adams County Fair Grounds near Henderson. The NOAA Lidar equipment was located at the Adams County Fair Grounds, approximately one mile north of Henderson.

Aircraft flights were made over the routes indicated on the map, Fig. 2 as Green 1, Green 2, and Green 3. These flights were by MRI carrying the TSI instrumentation. Spiral flights were also flown over Stanley Lake, Henderson and the EPA Trailer site. Flights were made on the days of November 14, 15, 16, 17, 20, and 21.

DESCRIPTION OF THE LIDAR SYSTEM[†]

A flexible remote sensing system has been developed in NOAA consisting of multiple wavelength laser transmitters and receivers with polarization sensitive detectors, a microwave radar, and a radiometer, mounted paraxially.

The transmitters, receiving telescope and detectors, are mounted in a trailer requiring a tractor for transport. The microwave radar, radiometer, sighting telescope, and a closed circuit TV viewer are mounted on the telescope mount.

The control center and data processing components are located in a van normally parked parallel to the trailer. The system is transportable but not mobile. It can be transported wherever roads are adequate. See Fig. 3.

Lidar Transmitter Characteristics

During the November 1973 experiment, only the second harmonic of the ruby laser radiation was emitted ($\lambda = 1/2 \times 697.3 \text{ nm}$).

* Continuous Air Monitoring of Pollution

[†] See Appendix for a brief discussion of light scatter from particles.

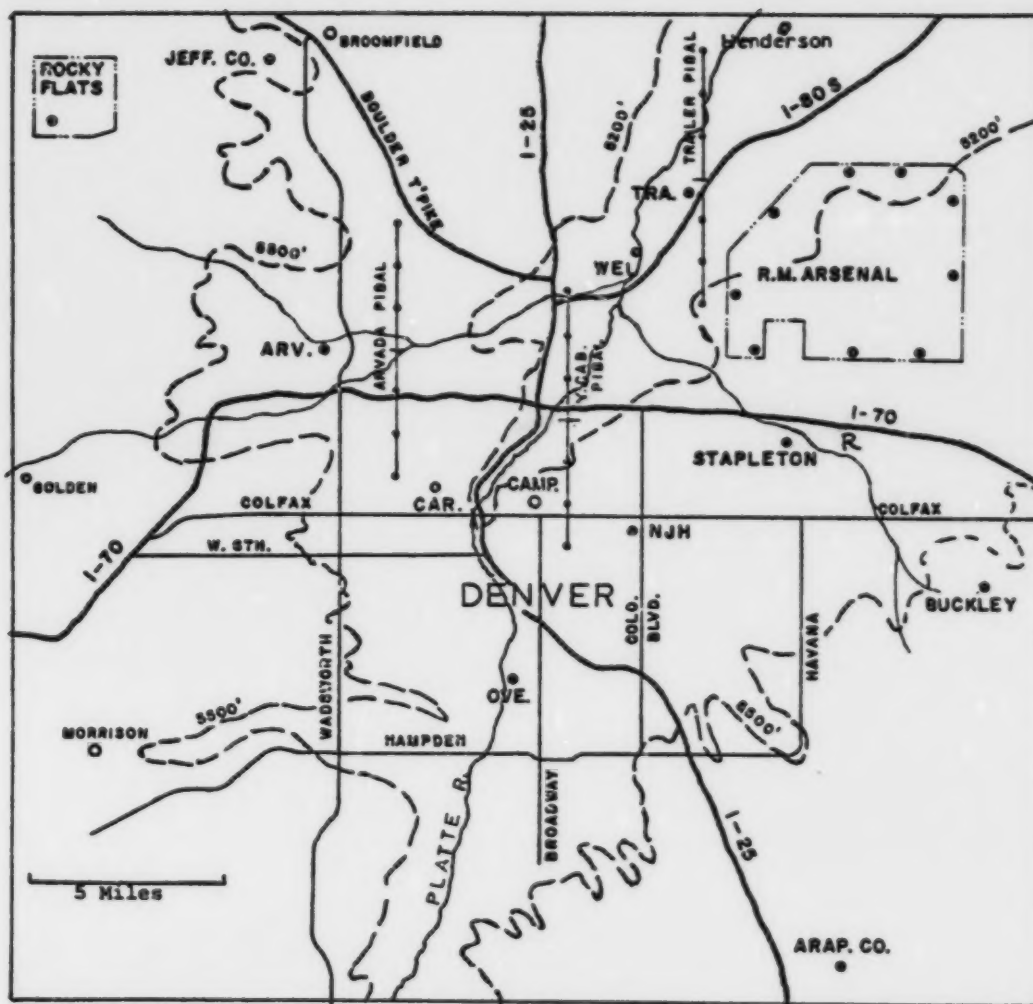


Fig. 1. Map of area covered in experiment.

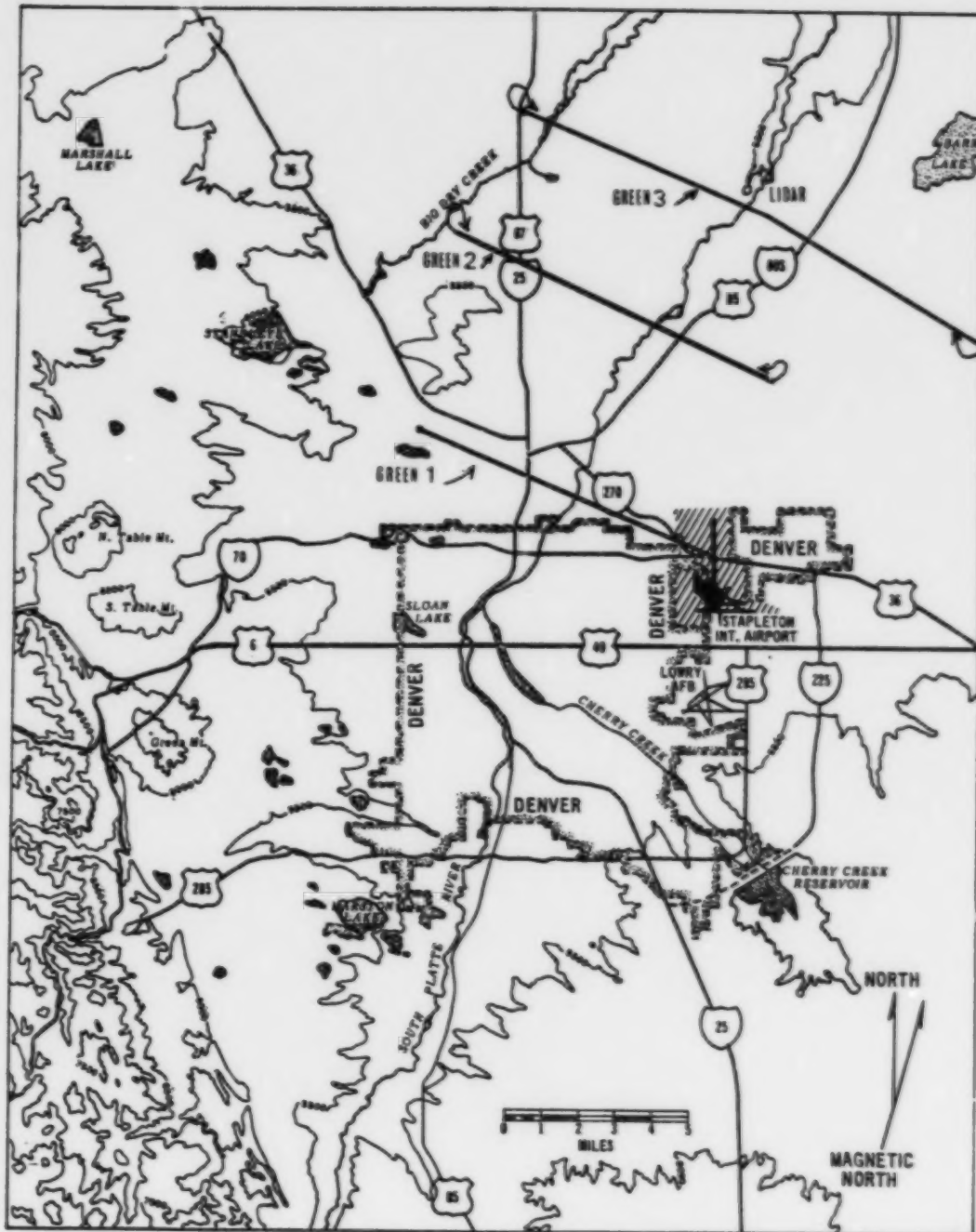


Fig. 2. Map showing general experiment area and flight paths.

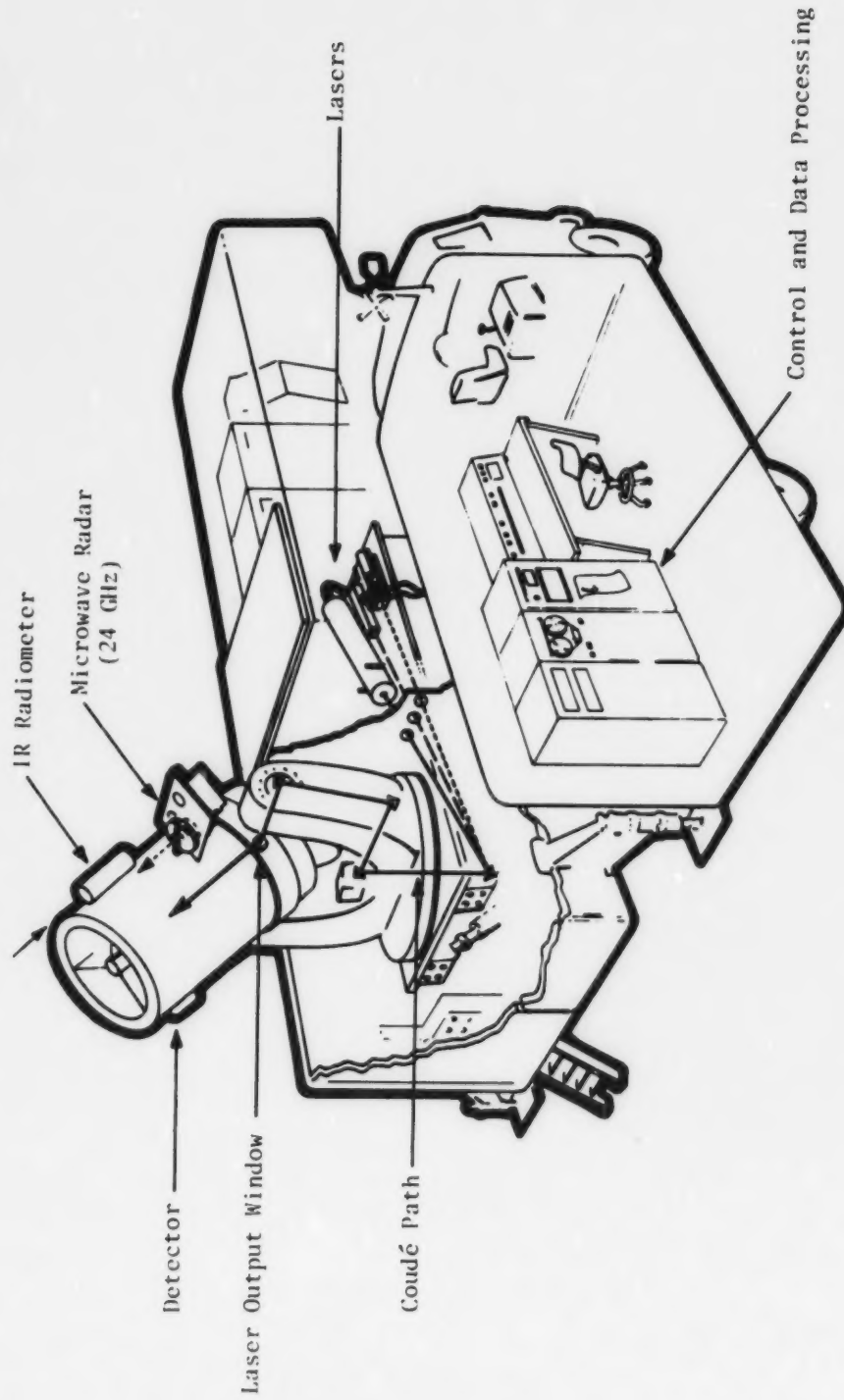


Fig. 3. Cut-away view of remote sensing facility.

Lidar Receiver Characteristics

The following are the most important characteristics of the receiver systems:

Telescope (Newtonian Mount)

Mirror Diameter 70 cm

Focal Length 203 cm

Telescope Mount - Converted NIKE-AJAX antenna mount.
One mil pointing accuracy, step and fast drives.

Detectors - Photomultipliers for optical and ultraviolet detection. Interference filters are used to limit receiving bandwidth and eliminate background radiation from the sky.

Data Processing Capability

The data processing system is shown in Fig. 4. The signal returns from the two photomultipliers are digitized and stored in two Biomation 8100 digitizers. When the laser is fired each unit digitizes and stores 2048 8-bit words at sample intervals as short as 10 nanoseconds. The contents of the digitizers are then transferred to the NOVA computer for processing and storage on a 9 track digital tape. The computer has a 24K word storage capacity, model 33 teletype terminal and a fast paper tape reader. A disc unit and CRT display will be added later. Along with the data, the system also records a number of bookkeeping quantities (laser power, time-of-day, telescope position, etc.). A total of 48 such quantities may be recorded.

Paralleling the computer data path is a standby system which can transfer raw data and bookkeeping quantities to tape in the event of a failure in the computer path.

DATA PROCESSING

The pollution study of November 1973 was a first trial of the new lidar equipment and the incomplete data recording system had several problems:

- (a) Only six binary digits (instead of eight) were available and occasionally the digitizer "hung up", that is, a straight line would be recorded until a relatively large change (a few units) produced a step.
- (b) Interference occasionally produced very narrow, large "spikes" on the record unrelated to the data.

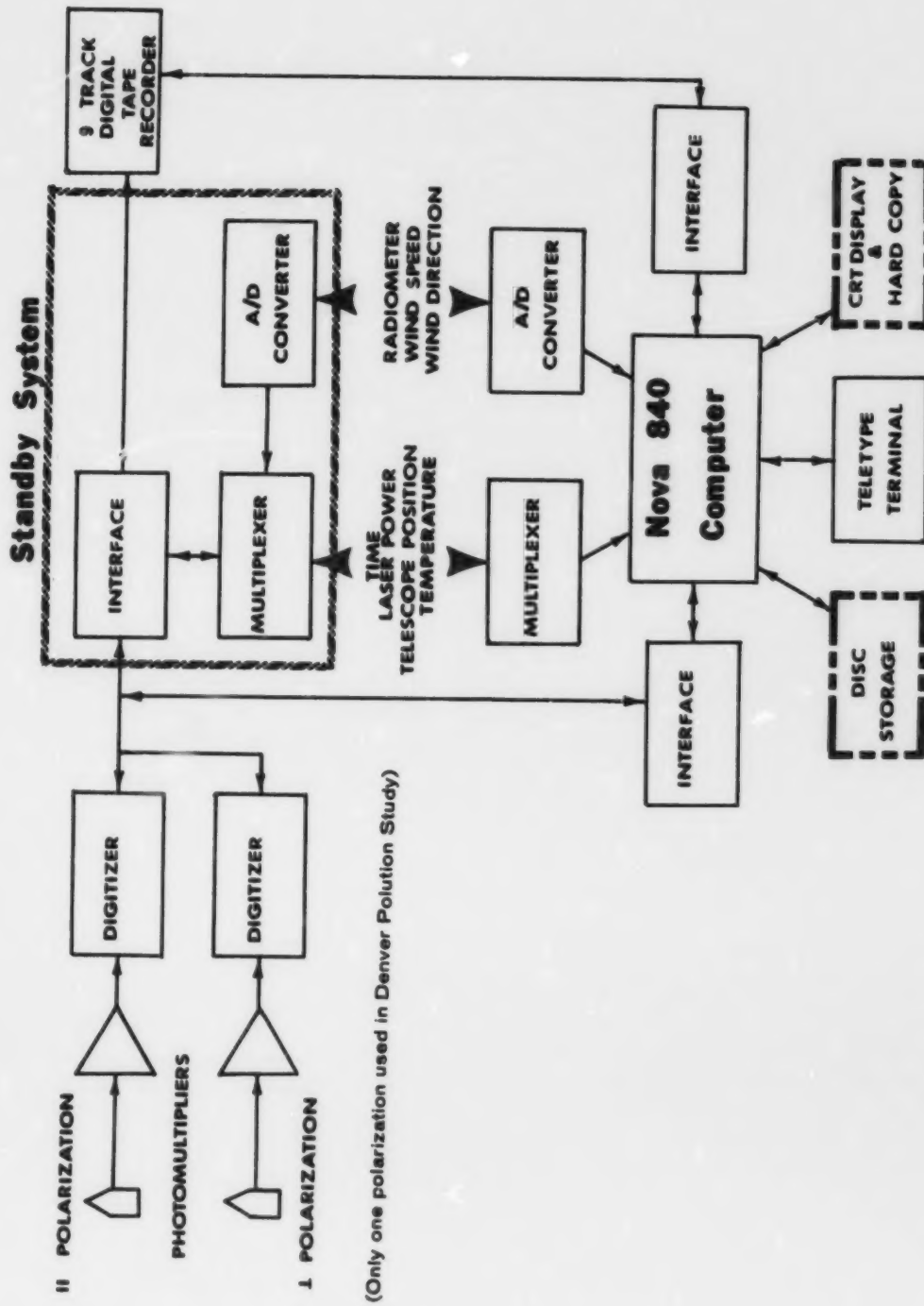


Fig. 4. Lidar data processing system.

- (c) The signal-to-noise ratio was adequate only up to 1200 m because of lack of circuitry to suppress the large signals from short ranges while raising the gain at longer ranges.

(The problems have all been removed in later experiments.) Because, in spite of these problems, much useful data are contained in the records, the data were processed to remove the first two problems. No way exists to recover the data when the signal is less than one integer of the full dynamic range of the digitizer (256 units), as is generally the case beyond 1200 m. Because, in most cases, the height of the temperature inversion, when it existed, was below 1200 m, there was little interest in the greater range.

Removing Instrumental Effects

Figure 5 shows examples of the problems mentioned above. Figure 6 shows the data after processing. The spikes of instrumental origin were always due to a single point having a large value compared with two adjacent points. They were removed by setting that "out-of-line" point to the average of the adjacent points.

The steps were caused by the tendency of the digitizer to "hang up", i.e., to retain a value until the signal changed by several units. They were removed, replacing them by a sloping straight line.

In addition to removing the instrumental noise, the baseline, due to instrumental bias, was subtracted, using an average of the last 200 points (the complete record contains 2000 points, sample interval .01 μ s). The data were then smoothed by a sliding average extending over 6 points or 60.0 ns, equivalent to the time constant of the receiver circuitry. The results of this partial data processing to remove instrumental effects are shown in Fig. 6. Complete data processing is shown, e.g., in Fig. 7.

Another instrumental effect, the cross-over effect, was not removed. The effect arose because the laser beam and the receiving telescope aperture are not coaxial; their axes are offset by 54 cm. Data was used only beyond the range where cross-over was complete (approximately 75 m). In some records noise of instrumental origin caused broad peaks near 900 m range. These have been removed, where identified.

One further instrumental effect that must be accounted for arises from the fluctuations of laser power output. Solid state lasers typically vary in power output for each shot by 5 to 10%. The power emitted on each shot was monitored and each signal (i.e., each record) divided by the approximate quantity. After this normalization and the other procedures outlined above to correct for instrumental effects, the data are recorded on a tape and are ready for scientific processing.

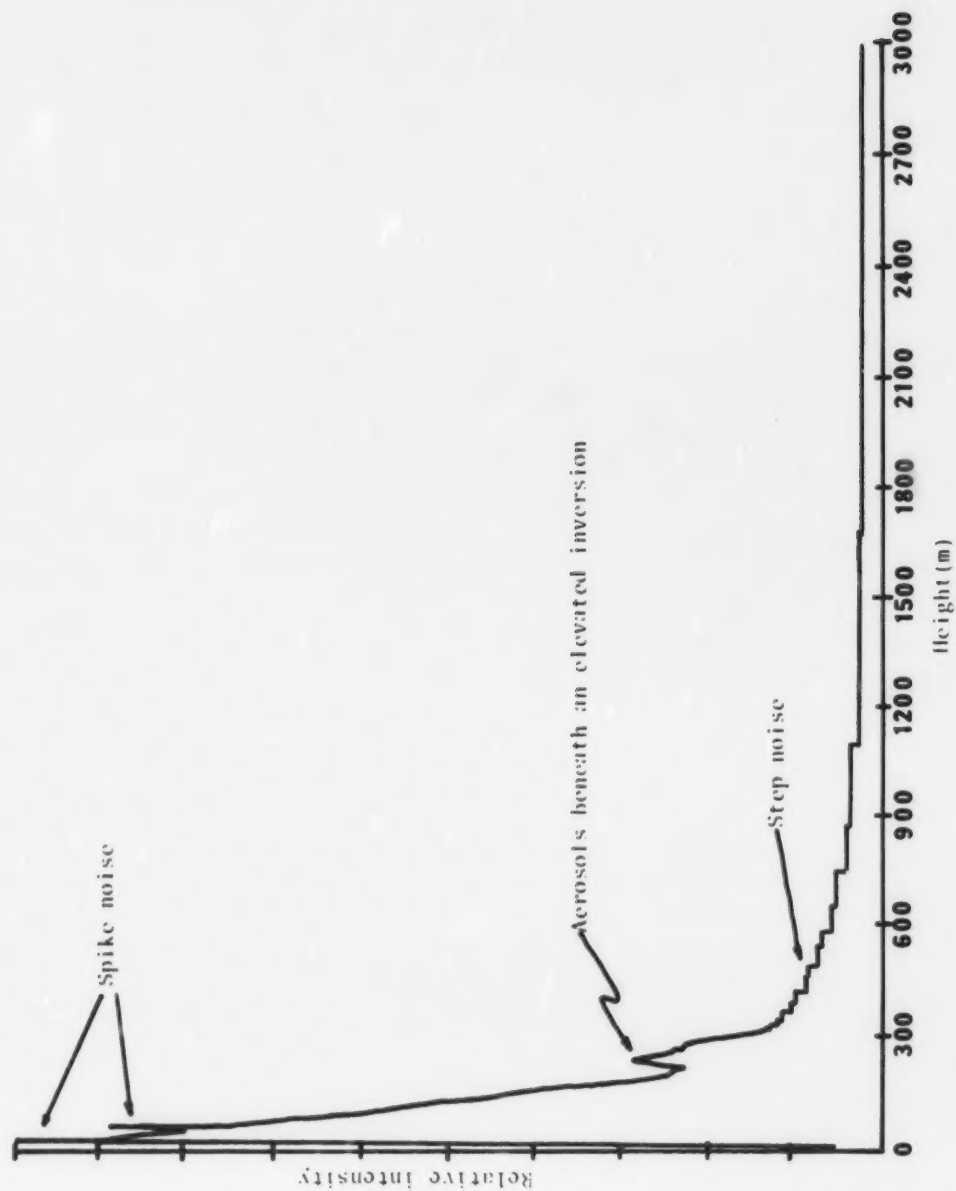


Fig. 5. Unprocessed data, Denver "Brown Cloud" experiment, November 1973, showing types of noise.

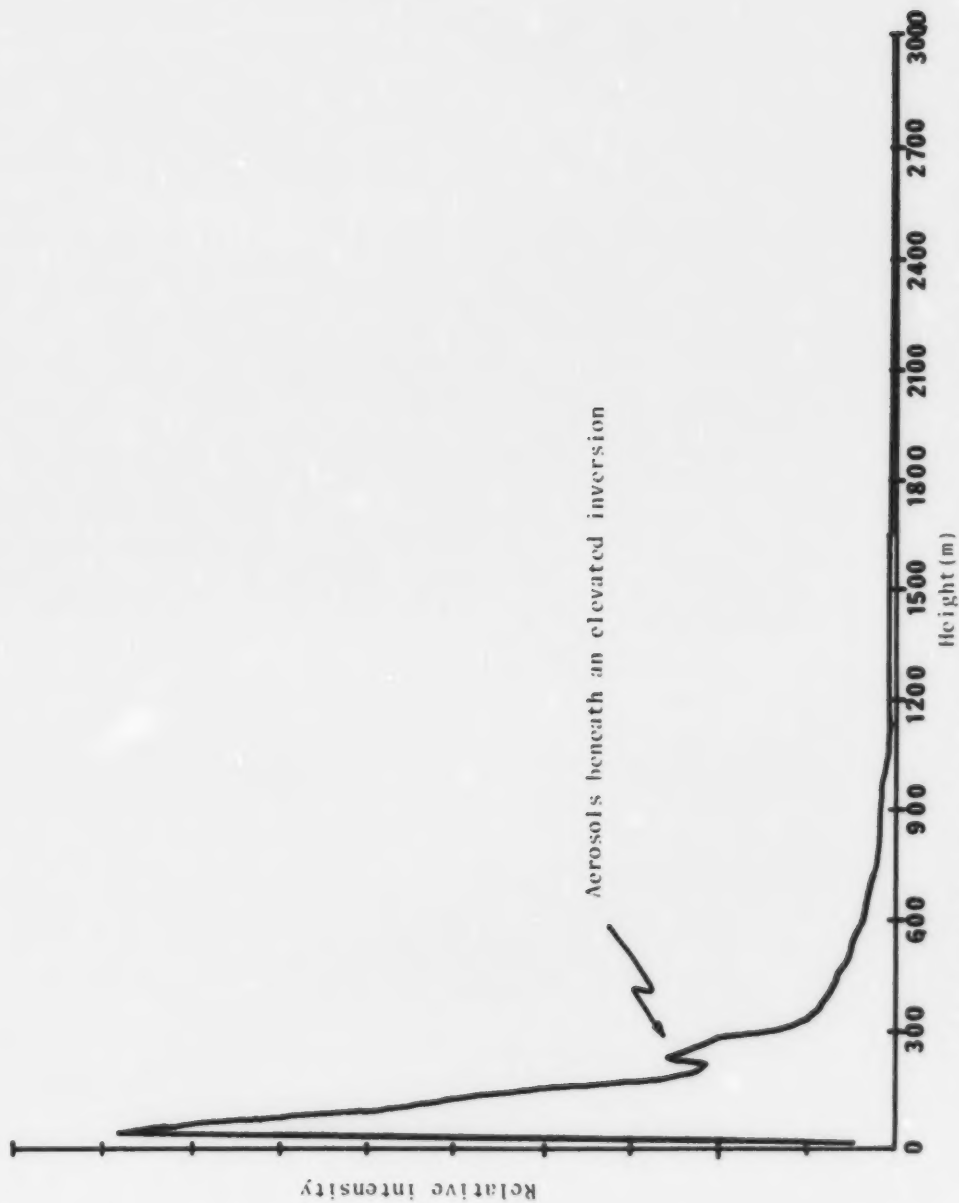


Fig. 6. Partially processed data, Denver "Brown Cloud" experiment, November 1973, with instrumental noise removed, baseline subtracted.

Scatter Cross Section as a Function of Range

The lidar signal from an extended target (say aerosols) is given by:

$$S = P_o \times (1/2) \times c \times \tau \times \beta' \times \frac{A}{4\pi R^2} \times f(R) \times t_R \times \exp(-2\sigma R),$$

where: S = signal power at detector

P_o = transmitted power

c = velocity of light

τ = lidar pulse width or receiver time constant, whichever is larger

R = range of aerosol scatterer (m)

β' = volume backscatter coefficient (m²/m³)

A = area of receiving telescope (m²)

f(R) = cross-over function

σ = total extinction coefficient (m⁻¹)

t_R = receiver efficiency

The quantity β' is the volume backscatter coefficient. We may neglect the exponential factor; at the small ranges and high visibility levels encountered in this experiment, the factor is nearly one. In order to determine β' it is necessary to know the other factors. The factors c, τ, P_o, A, and R are determinable with satisfactory accuracy. The quantity S requires a calibration of detector sensitivity and electronic gain. These are made uncertain by temperature, aging and equipment drift and modification. The function f(R), due to the beam cross-over geometry, is difficult to evaluate because of variation of temporal and spatial power density across the laser beam. Further, t_R, the receiver efficiency, is difficult to measure satisfactorily and may vary with time as optical surfaces age and become dirty.

There are a number of ways lidar signals may be calibrated, e.g.,

- (a) absolute calibration against a target whose scatter characteristics are known.
- (b) evaluate and stabilize the characteristics of the optical and electronic systems.

- (c) use the Rayleigh scatter from the "clear air" for a target as in (a) above.
- (d) determine the aerosol concentration at short range by a ground-based instrument, and estimate aerosol concentrations at greater ranges from the relative intensity.
- (e) if a clear day occurred, assume it was Rayleigh scattering, neglecting a small error, and for each value of the range determine the ratio of all other signals to that chosen signal.

We here choose a combination of the last two methods because of their simplicity and because the quality of the data does not warrant more complicated procedures. Specifically, the signal from clearest days as shown by ground based aerosol characterization facilities was chosen to represent Rayleigh scattering. (An estimate, based on particle counts, showed less than 15% error arising from this assumption at ground level.) Ratios were formed, for each range, of other signals to the chosen standard. Methods (d) and (e) are useful in estimating the number concentration of particles only if the size distribution and chemical constitution do not change radically over the range of interest. When data from aircraft flights were available, the distributions were found to be approximately constant with height, as discussed in the next section.

A possible flaw in this method is that data for choosing the standard "clear" day was available only from ground based nephelometer units. Thus, even if the air were properly chosen as "clear" at ground level, it may not have been "clear" at higher levels. This source of error was minimized by choosing records whose ratio to a calculated Rayleigh scatter signal changed minimally with height.

Averages of the backscatter coefficient over space and time are described in the following section.

OBSERVATIONS

Observations were made by lidar, by ground based instruments and by aircraft. We present here the results of lidar observations and summarize the available data from ground units located near the lidar and aircraft runs in the vicinity. The section concludes with a discussion of the lidar measurements compared with other data.

Lidar Observations

Many of the lidar signals show significant aerosol content above temperature inversions. Superficially, the inversion is considered to "put a lid" on the lower atmosphere, preventing vertical mixing of pollution. That picture is, of course, often accurate, but in the

Denver area, during these observations, the atmosphere immediately above the inversion often had aerosols with as much backscatter intensity as below, after correction for $1/R^2$. There has been some evidence of mixing through inversions, but in this case it is suspected that the aerosols were advected from distant sources, emitted at earlier times, and were either in place before the formation of the temperature inversion, or it is possible that a wind above the inversion level may have brought the aerosols over the lidar area at night, when the lower level winds are calm, from other parts of the city. Because of the limited range of the lidar as employed at that time, the upper level of the aerosols was not always observed. In some models of aerosol concentration and diffusion, the temperature inversion level is chosen as the top of the volume in which aerosols are mixed. Clearly, this could lead to inaccurate estimates of total pollutants in the atmosphere. Those remote sensing devices which detect the temperature inversion levels (e.g., acoustic sounder, FM/CW radar) thus do not always provide accurate information on the height of particulates. The lidar is backscattered principally by particulate matter.

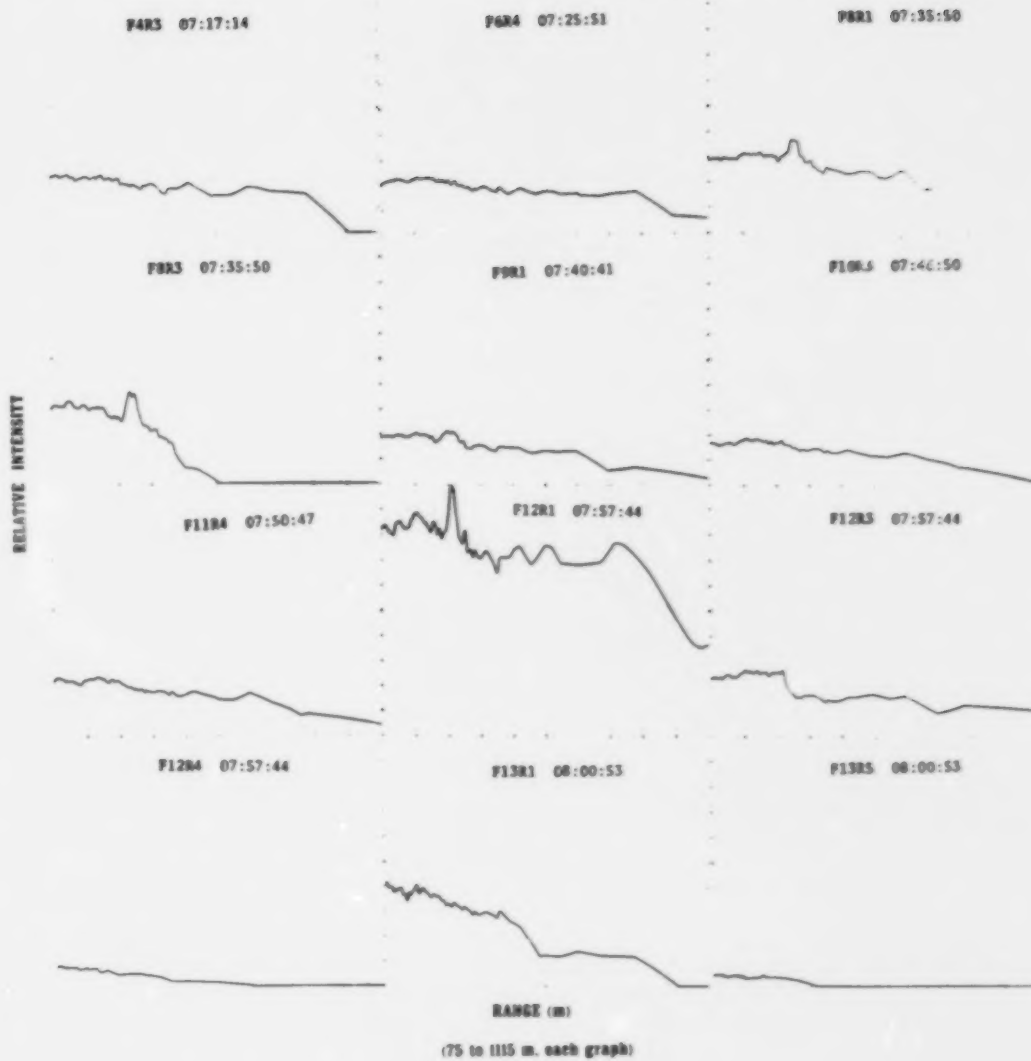
The relative backscatter radiance* of the aerosols is presented as a function of height in Figs. 7 to 10. Each graph results from a single lidar shot. Each is marked with the approximate time of the shot (MST) and the date. Shots with the same time indication were taken at different but closely spaced actual times and are among those averaged for a given entry under that time in Tables 2 to 5. The horizontal axis is the height (m) and extends from 75 to 1115 m. The backscatter radiance on the vertical axis has been multiplied by a convenient factor to accommodate it to the available space; the factor is constant for each day. When multiplied by the appropriate factor the graphs are approximately the backscatter radiance for each day; because of the lack of absolute standards and the possibility of calibration drifts, the backscatter radiance during the day may be considered consistent, but the values are only approximately related between days.

The height was divided into four sections of 260 m and the average backscatter radiance obtained for each. These averages and the average over the total height are presented in Tables 2 to 5. No scale factors are presented in this data and, within the limitations mentioned above, the numbers in the tables represent the average relative backscatter radiance.

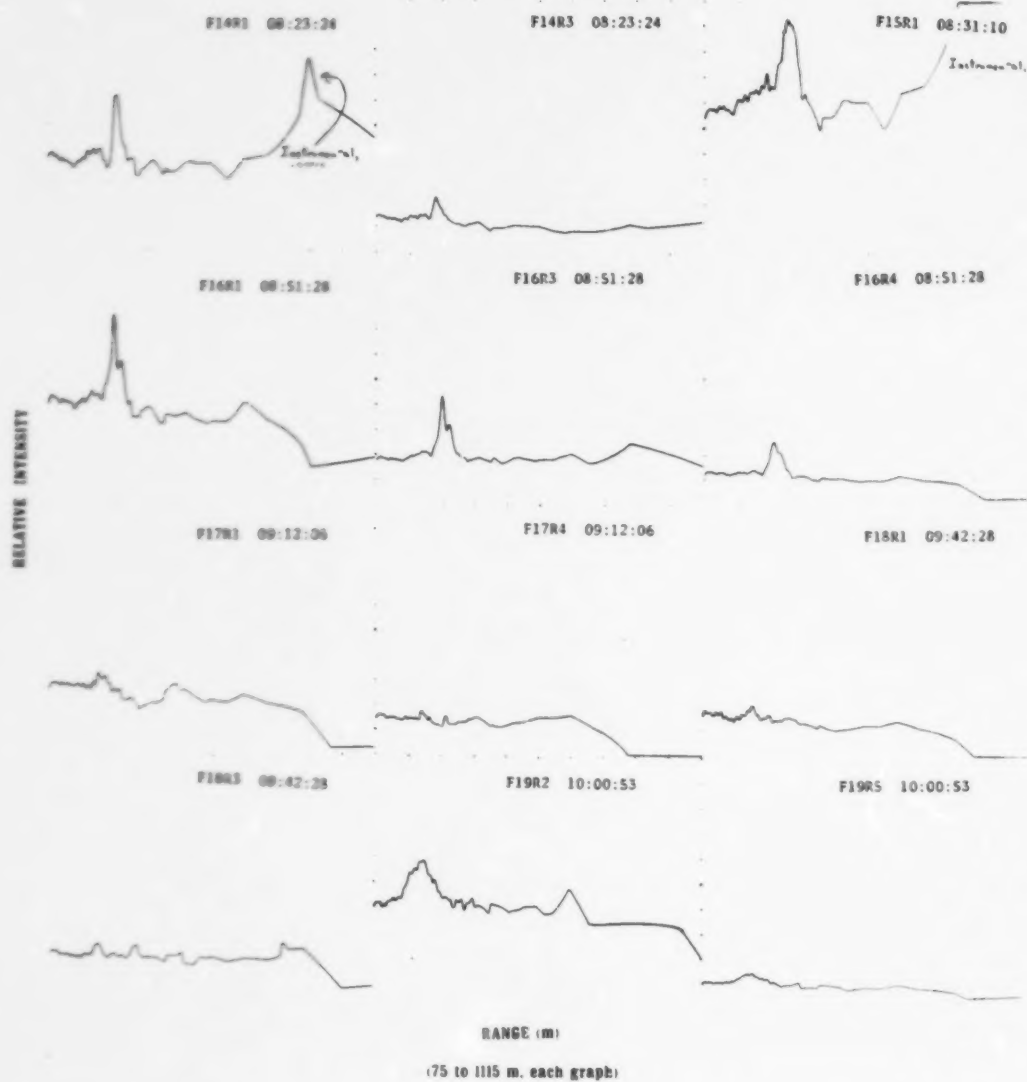
By utilizing aerosol measurement data from nearby observations we may approximately calibrate the lidar signals in terms of the number concentration if the size distribution and index of refraction distribution remain approximately constant. An examination of aircraft data shows that the relative size distribution varies little as a function of altitude during the course of any one day. (The number concentration varies considerably as a function of altitude.) More precisely, based on data from this and other observations, if the meteorological conditions are calm and remain approximately the same, during the course of a day or a few days, the relative size distribution does not change much,

* See Appendix

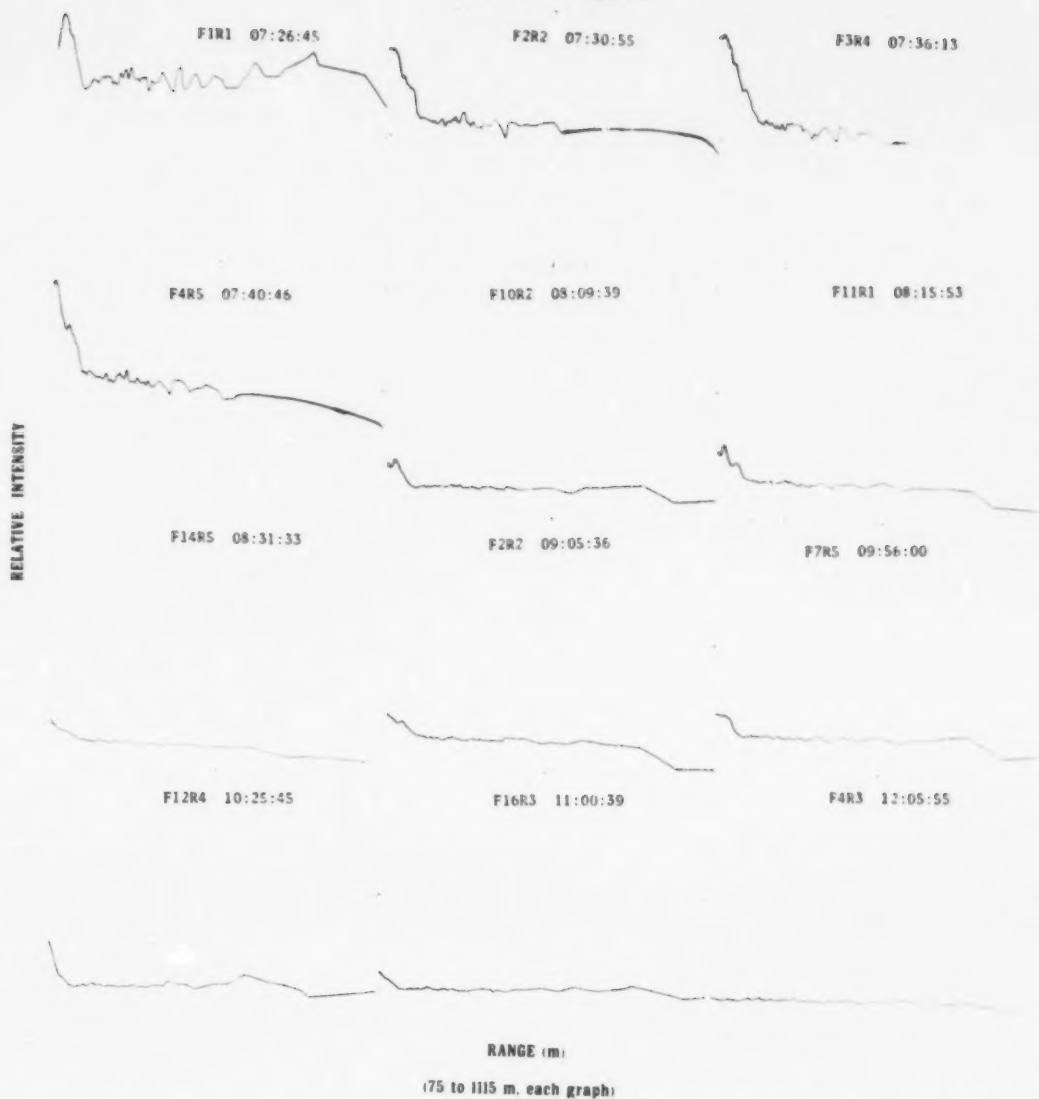
Nov. 18, 1973 Figure 7A



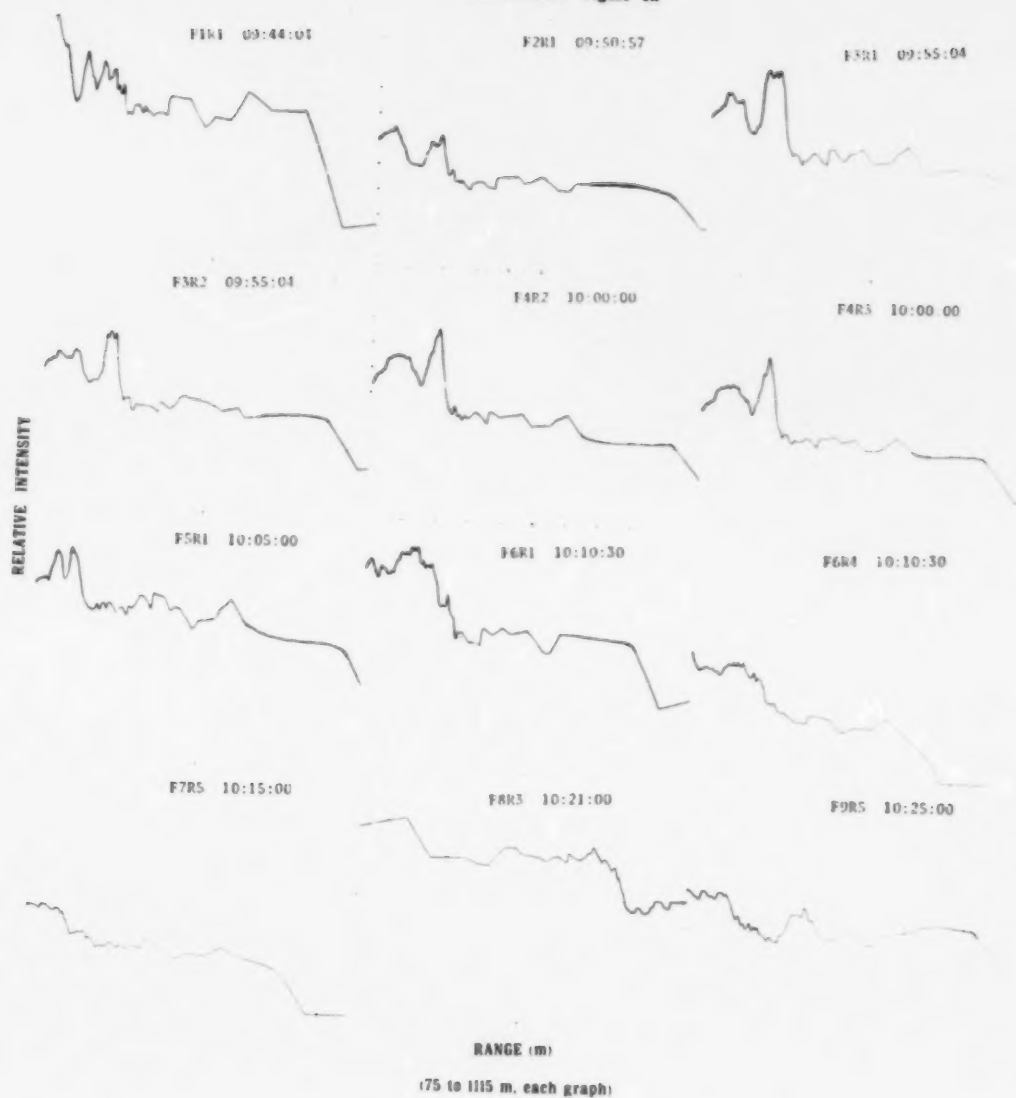
Nov. 16, 1973 Figure 7B



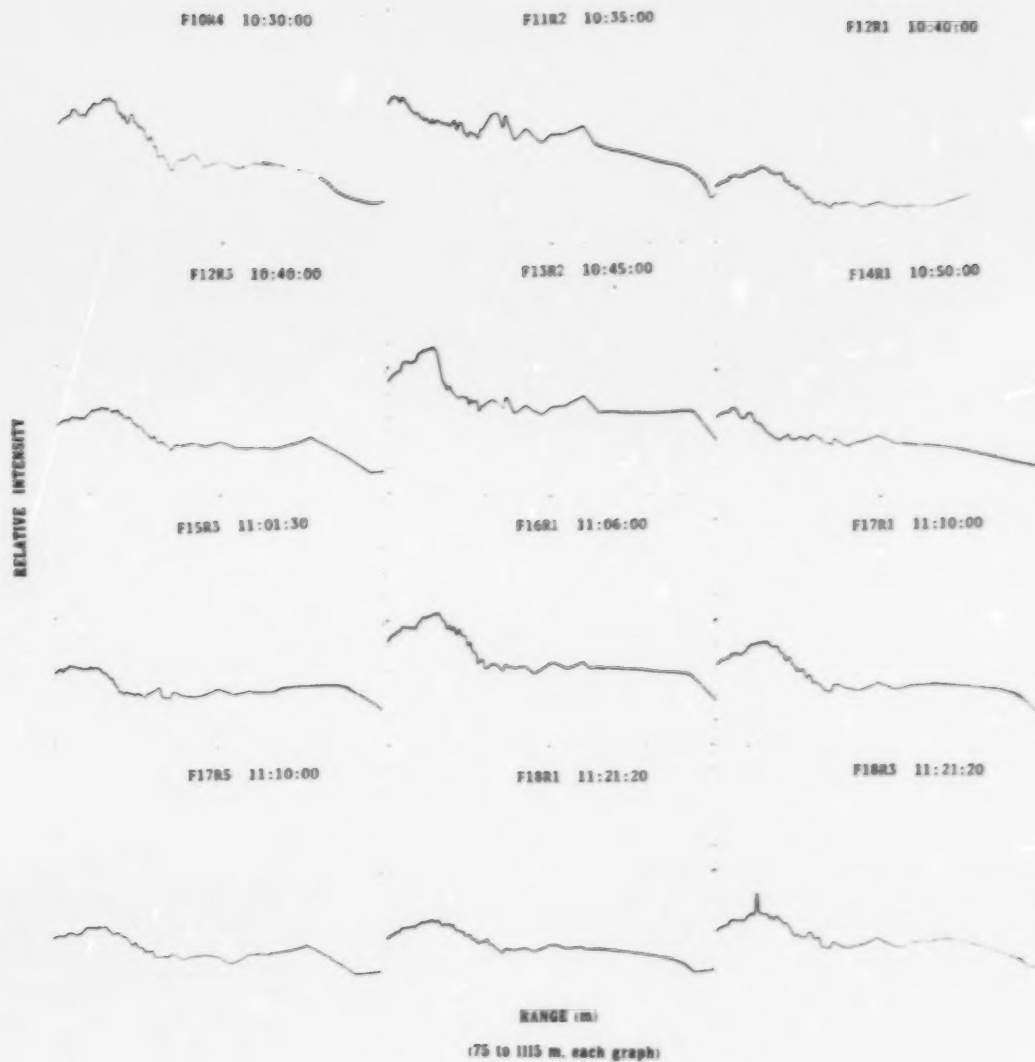
Nov. 21, 1973 Figure 8



Nov. 26, 1973 Figure 9A



Nov. 26, 1973 Figure 9B



Nov. 29, 1973 Figure 10

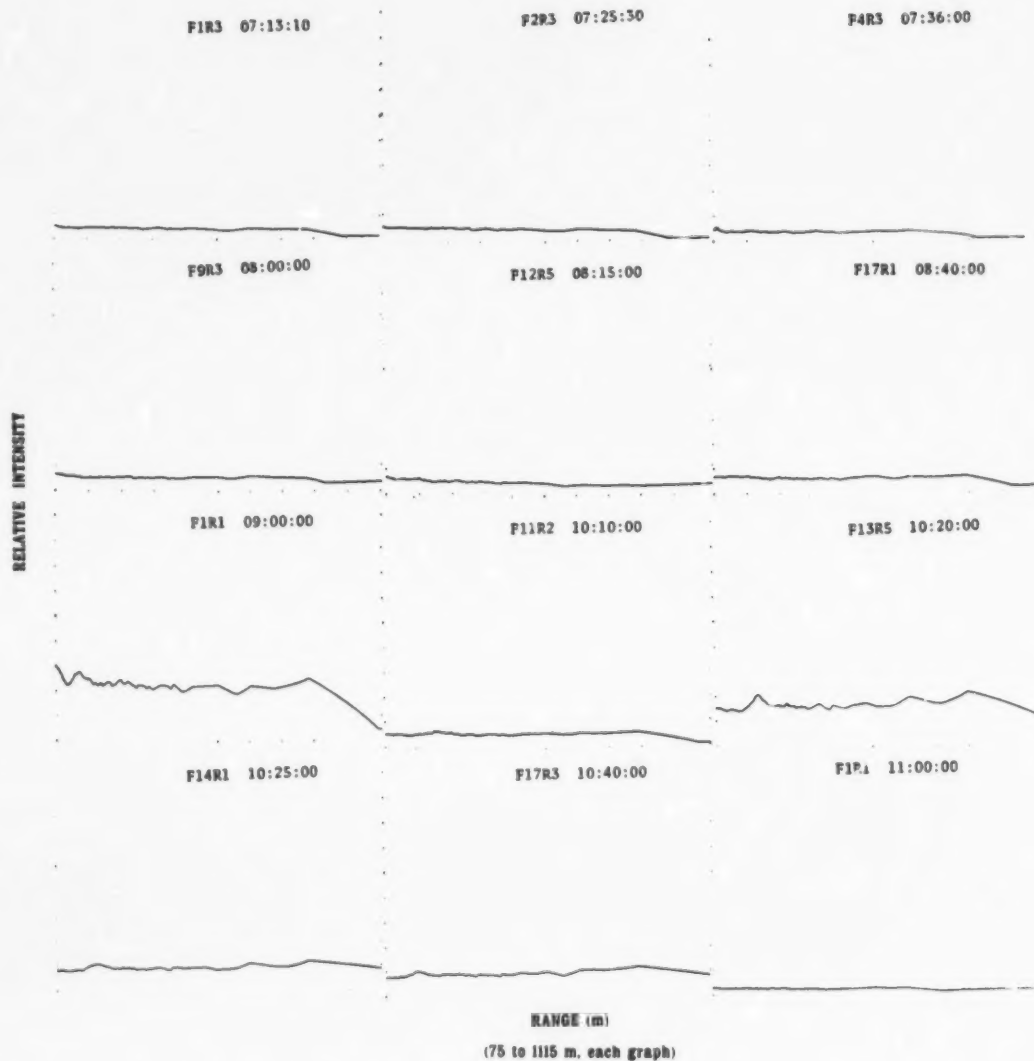


Table 2.
AVERAGE RELATIVE BACKSCATTER RADIANCE
(Nov. 16, 1973)
HEIGHT INTERVALS (M)

DAY	TIME	75- 335	335- 575	575- 855	855- 1115	75- 1115
J20	07:01:14	14.00	13.45	14.16	15.01	14.15
J20	07:06:48	12.97	11.98	12.55	14.69	13.05
J20	07:10:50	19.33	17.14	16.68	17.25	17.60
J20	07:17:14	14.77	13.37	14.28	14.58	14.25
J20	07:22:43	14.74	14.15	15.72	17.96	15.69
J20	07:25:51	15.42	13.63	13.33	12.77	13.79
J20	07:35:50	14.28	11.38	9.75	9.07	11.12
J20	07:40:41	15.65	13.43	13.40	13.17	13.91
J20	07:46:50	14.50	12.45	12.97	12.92	13.21
J20	07:50:47	16.97	14.12	13.79	14.09	14.75
J20	07:57:44	19.86	15.96	16.11	17.76	17.42
J20	08:00:53	9.92	7.56	5.67	4.61	6.94
J20	08:23:24	10.55	8.92	9.64	14.38	10.87
J20	08:31:10	20.87	20.27	22.45	33.89	24.37
J20	08:51:28	11.69	8.95	8.67	5.67	8.75
J20	09:12:06	11.52	9.81	9.31	3.35	8.50
J20	09:42:28	10.34	9.16	9.02	7.33	8.96
J20	10:00:53	17.17	14.75	15.30	15.40	15.66

Table 3.
AVERAGE RELATIVE BACKSCATTER RADIANCE
(Nov. 21, 1973)
HEIGHT INTERVALS (M)

DAY	TIME	75- 335	335- 555	555- 855	855- 1115	75- 1115
325	07:26:45	1.02	0.22	0.31	0.38	0.50
325	07:30:55	1.91	0.59	1.05	1.28	1.32
325	07:36:13	0.17	1.84	1.98	0.34	0.23
325	07:40:40	0.21	1.36	1.50	1.90	1.74
325	08:06:12	1.07	0.88	0.83	0.61	0.85
325	08:09:39	1.05	0.90	0.88	0.70	0.89
325	08:15:53	1.23	0.97	0.93	0.55	0.92
325	08:20:51	1.01	0.83	0.78	0.54	0.79
325	08:26:34	1.06	0.81	0.68	0.36	0.75
325	08:31:35	1.05	0.82	0.62	0.34	0.71
325	09:00:45	1.39	1.12	1.17	1.01	1.17
325	09:05:38	0.94	0.74	0.68	0.19	0.64
325	09:10:34	1.16	0.95	0.87	0.65	0.91
325	09:12:05	1.23	1.10	1.27	1.40	1.27
325	09:32:32	1.22	0.97	0.97	0.78	0.98
325	09:47:55	0.98	0.77	0.79	0.32	0.72
325	09:56:00	1.34	1.14	1.14	0.83	1.11
325	10:25:45	1.41	1.27	1.27	0.99	1.24
325	10:41:54	1.56	1.74	1.85	2.10	1.81
325	10:43:55	1.36	1.34	1.42	1.44	1.39
325	10:51:38	1.19	1.13	1.11	0.85	1.07
325	11:00:39	1.42	1.28	1.33	1.32	1.34
325	11:16:02	1.25	1.18	1.22	1.19	1.21
325	11:36:15	1.19	1.24	1.34	1.37	1.29
325	11:48:17	.97	.90	.98	1.06	.99
325	12:05:55	1.05	1.04	1.06	1.04	1.05
325	12:33:35	.75	.60	.69	.75	.71

Table 4.
AVERAGE RELATIVE BACKSCATTER RADIANCE
(Nov. 26, 1973)
HEIGHT INTERVALS (M)

DAY	TIME	75- 335	335- 595	595- 855	855- 1115	75- 1115
330	09:44:04	9.46	7.59	7.53	3.75	7.08
330	09:50:57	9.26	7.35	7.46	7.20	7.82
330	09:55:04	10.72	7.73	7.59	6.97	8.25
330	10:00:00	10.82	7.41	7.06	6.16	7.86
330	10:05:00	8.93	7.96	7.88	7.59	8.09
330	10:10:30	11.02	7.68	6.89	4.65	7.71
330	10:15:00	10.57	8.65	8.91	7.37	8.83
330	10:21:00	11.85	8.27	8.58	6.73	8.85
330	10:25:00	10.23	8.77	8.85	8.64	9.12
330	10:30:00	11.00	7.52	7.07	6.14	8.08
330	10:35:00	8.76	7.70	7.86	7.99	8.08
330	10:40:00	5.89	3.90	3.72	3.42	4.23
330	10:45:00	6.08	4.20	5.11	5.38	5.49
330	10:50:00	5.09	4.00	4.28	3.79	4.29
330	11:01:30	5.41	4.05	4.37	4.29	4.53
330	11:06:00	6.48	4.41	4.59	4.32	4.95
330	11:10:00	6.28	4.16	4.24	3.55	4.56
330	11:21:20	5.55	3.41	3.95	3.29	4.18

Table 5.
AVERAGE RELATIVE BACKSCATTER RADIANCE
(Nov. 29, 1973)
HEIGHT INTERVALS (M)

DAY	TIME	75- 335	335- 595	595- 855	855- 1115	75- 1115
333	07:13:10	0.97	0.89	0.90	0.65	0.85
333	07:25:30	1.11	1.05	1.03	0.96	1.04
333	07:30:45	0.90	0.83	0.85	0.66	0.81
333	07:36:00	1.02	0.93	0.92	0.81	0.92
333	07:40:00	0.84	0.75	0.74	0.54	0.72
333	07:45:00	1.09	1.01	1.03	0.96	1.02
333	07:50:00	1.17	1.05	1.01	0.74	0.99
333	07:55:00	0.81	0.73	0.72	0.58	0.71
333	08:00:00	0.91	0.82	0.84	0.73	0.82
333	08:05:00	0.89	0.81	0.81	0.64	0.79
333	08:10:00	1.08	0.95	0.88	0.54	0.86
333	08:15:00	1.18	1.02	0.94	0.76	0.98
333	08:20:00	0.97	0.86	0.81	0.61	0.81
333	08:25:00	0.57	0.16	0.00	0.00	0.18
333	08:30:00	0.17	0.00	0.00	0.00	0.04
333	08:35:20	1.67	1.44	1.45	1.10	1.43
333	08:40:00	0.79	0.68	0.65	0.46	0.65
333	08:45:30	1.48	1.24	1.23	0.79	1.18
333	08:50:00	1.04	0.84	0.78	0.30	0.74
333	08:55:00	0.92	0.78	0.78	0.50	0.75
333	09:00:00	2.65	2.44	2.44	2.16	2.42
333	09:15:00	0.96	0.89	0.94	0.69	0.88
333	09:30:00	1.19	1.18	1.27	1.33	1.24
333	09:35:00	1.05	1.08	1.18	1.27	1.15
333	09:40:00	1.10	1.11	1.21	1.35	1.20
333	09:45:05	1.22	1.19	1.25	1.37	1.27
333	09:50:02	1.13	1.14	1.22	1.28	1.19
333	09:55:00	1.09	1.13	1.25	1.41	1.22
333	10:00:00	0.90	0.82	0.84	0.70	0.82
333	10:05:00	1.02	1.00	1.06	1.06	1.03
333	10:10:00	1.25	1.15	1.21	1.24	1.22
333	10:15:00	0.89	0.79	0.78	0.65	0.78

Table 5. (cont.)
 AVERAGE RELATIVE BACKSCATTER RADIANCE
 (Nov. 29, 1973)
 HEIGHT INTERVALS (M)

DAY	TIME	75- 335	335- 555	555- 855	855- 1115	75- 1115
333	10:20:00	1.10	1.05	1.10	1.02	1.07
333	10:25:00	1.32	1.33	1.45	1.55	1.41
333	10:30:00	1.32	1.33	1.42	1.46	1.36
333	10:35:00	1.31	1.26	1.36	1.32	1.31
333	10:40:00	1.24	1.23	1.37	1.36	1.30
333	10:45:00	1.24	1.25	1.34	1.31	1.28
333	10:50:00	1.25	1.23	1.34	1.41	1.31
333	10:55:00	1.06	1.06	1.14	1.18	1.12
333	11:00:00	1.13	1.14	1.17	1.11	1.14
333	11:05:00	1.28	1.21	1.26	1.27	1.26
333	11:10:00	1.12	1.44	2.15	3.34	2.01
333	11:15:00	1.26	1.25	1.22	1.21	1.23
333	11:20:00	1.07	0.95	0.53	1.16	0.93
333	11:25:04	1.28	1.22	1.27	1.31	1.27
333	11:30:00	1.18	1.10	1.15	1.14	1.14

in a given location, as a function of altitude, to the top of the mixed layer. Under these circumstances a calibration of the lidar backscatter signal is permissible by reference each day to ground based particle measuring equipment. The total loading in micrograms per meter at the ground should be applied to the backscatter radiance in the 75-335 m height interval. Correction for the volume of the lidar beam may be deduced from its initial diameter (5.08 cm) and its divergence (2 mrad). The total particulate loading of the atmosphere up to 1115 m may be calculated from this data. See Appendix for the method. Calculations are not included here because of the unavailability of ground based data to the author.

Ground Based Observations

Although the lidar van was located at the Adams County Fair Grounds, the nearest location where meteorological data of interest was taken on days when the lidar was operating was at the Denver Trout Farm (DUFFFARM) on the 16th and 21st of November 1973. The significant measurements were the wind data (speed and direction) and backscatter data measured by an integrating nephelometer. Plots of these data as a function of time for these two days are shown in Figs. 11 and 12. Along the left ordinate is the scale for the wind speed in km-hr^{-1} . The scale for scattering in units of 10^{-4}m^{-1} is along the right hand ordinate. The measurements on the 16th cover the entire 24-hour period. On the 21st the wind became strong at about 1600 hrs blowing the pollutant cloud away so measurements were discontinued. The data were given as averages over one hour intervals so horizontal lines were drawn on the graph covering the one hour interval. Light solid lines connect the wind data points; dashed lines connect the backscatter points. The wind direction is written in at each point. The total pollutant load for November 16 (0000-2400 hr) was $41.5 \mu\text{g}/\text{m}^3$; for November 21 (0000-1600) the load was $32 \mu\text{g}/\text{m}^3$ as measured by an 8-stage Anderson sampler.

Aircraft Observations

In addition to the ground based measurements, observations by an instrumented aircraft over designated flight patterns were made. The one of particular interest to the lidar observations is the one referred to as the Henderson spiral. The aircraft circled over the Henderson site taking data as it spiraled, thus getting an altitude profile for the various measurements. The profiles of particular interest for analysis of the lidar measurements were the backscatter coefficients obtained by an integrating nephelometer (10^{-4}m^{-1}), the temperature (C) and condensation nuclei concentration, CN, (10^4cm^{-3}). The available data for 16 November and 21 November are presented in Figs. 13, 14, and 15 at the times shown. Appropriate scales for the three quantities are indicated by b_{scat} for the scattering coefficient, T for temperature, and X for condensation nuclei. The altitude in hundreds of feet (MSL) is plotted along the ordinate starting at 5000 ft (ground level is 5151 ft).

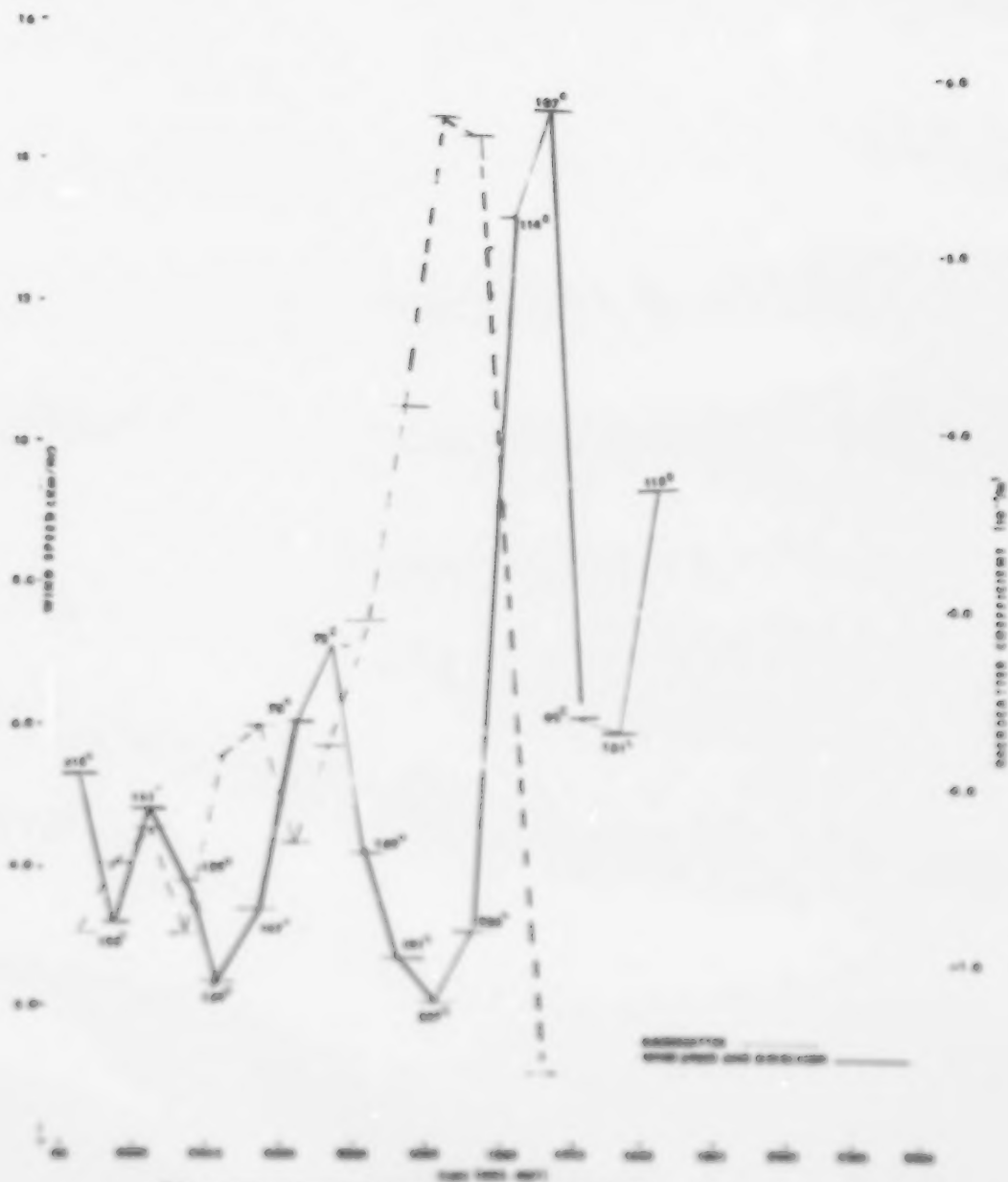


Fig. 11. Viscosity and temperature dependence of the polymer.

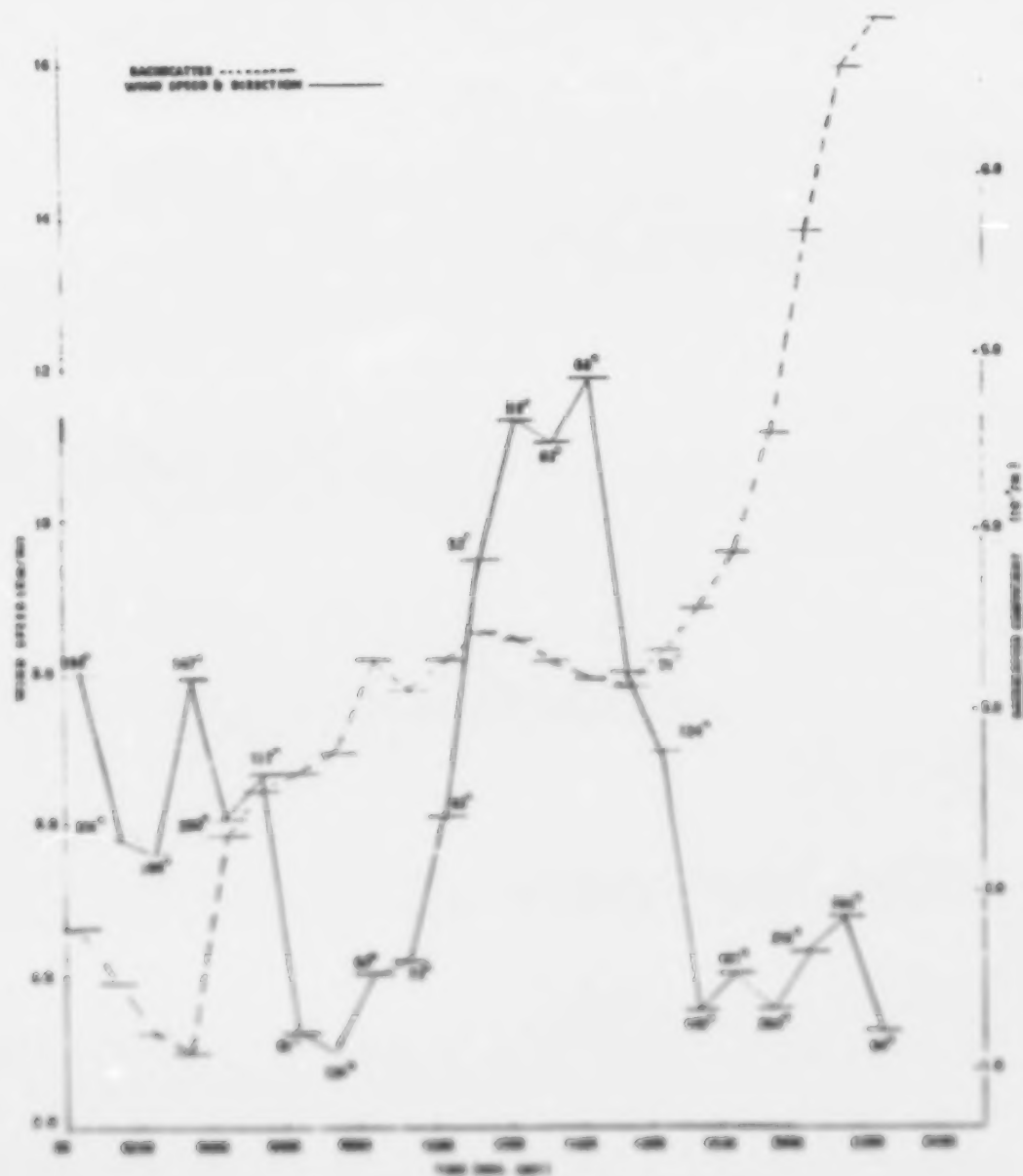


Fig. 12. Wind speed and direction data for station 10, December 1971



Fig. 15. Aircraft data (Munderson Spiral) ending 13:01 TST 16 November 1973.

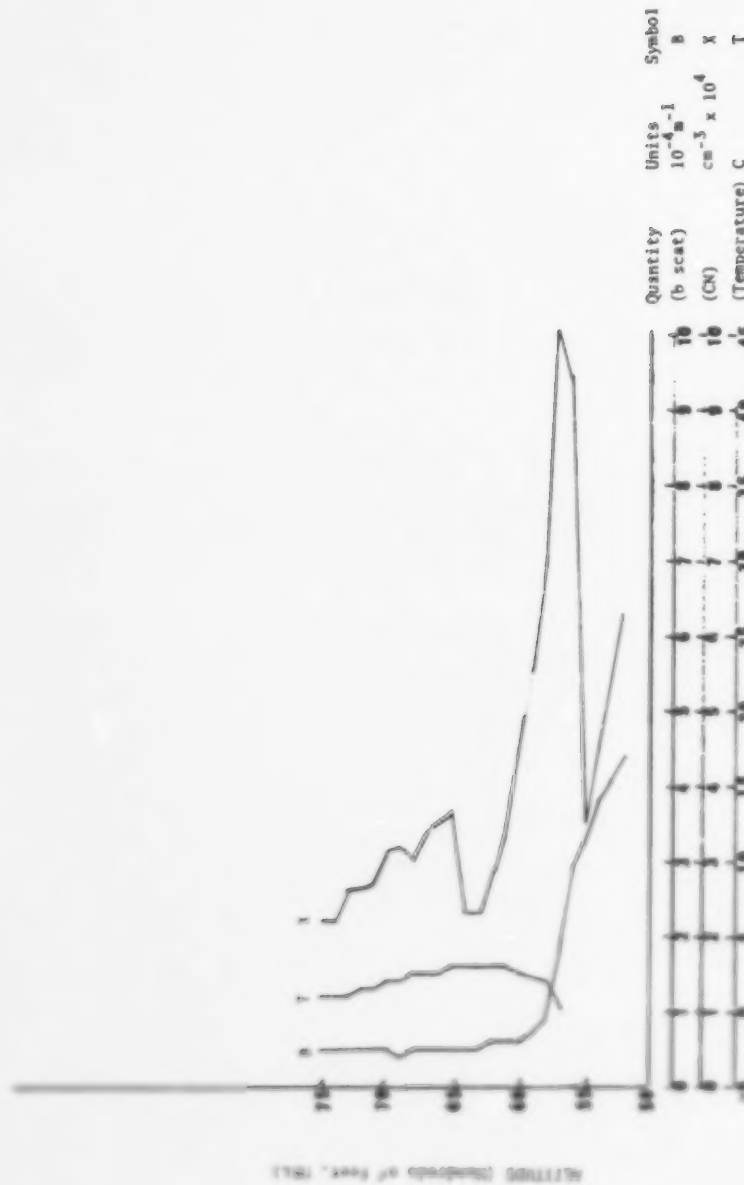


Fig. 14. Aircraft data (Henderson Spiral) ending 9:15 MST 21 November 1973.

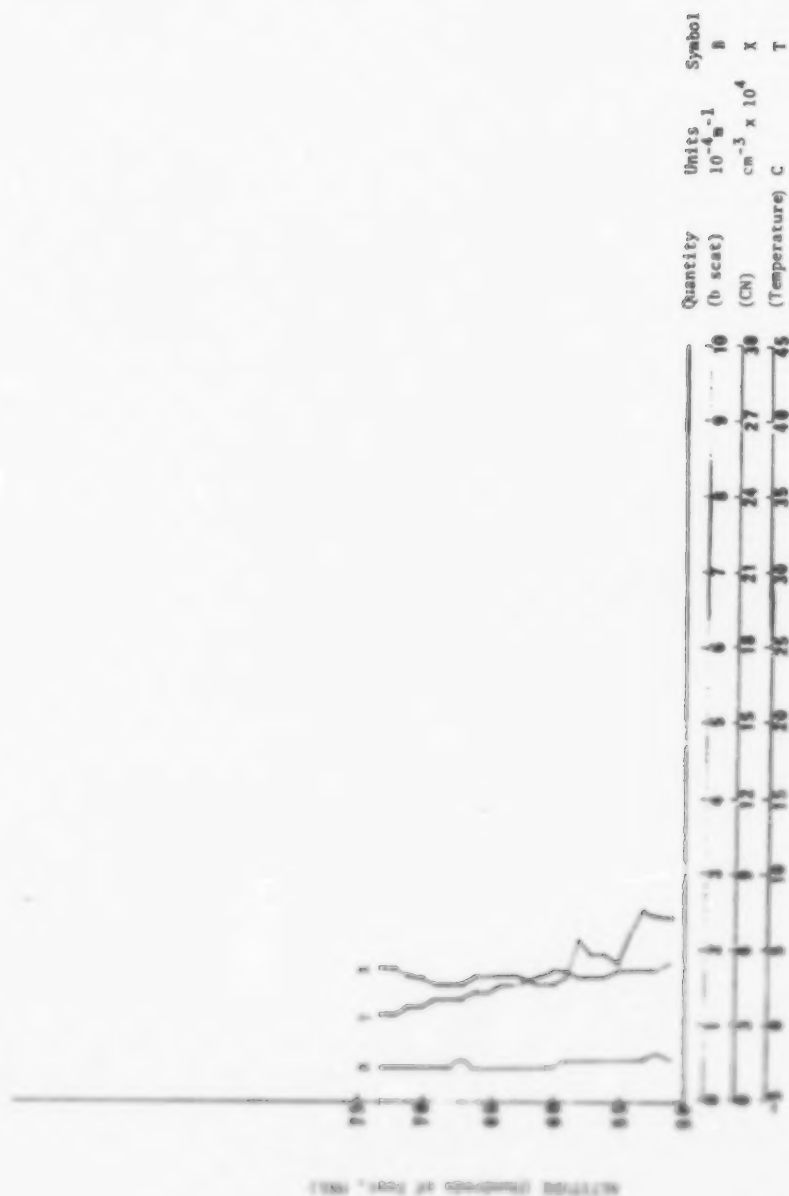


Fig. 15. Aircraft data (Henderson Spiral) ending 12:34 PST 21 November 1973.

At the time of the morning flight on 21 November there was a very distinct layer of pollution between 5500 and 6000 ft and a less pronounced one starting at about 6500 ft (Fig. 14). These layers are just barely distinguishable in the data from the noon time flight (Fig. 15).

Discussion of Lidar Observations

Four days of data are discussed below. During those days the lidar was active. On 16, 21, November, data from the aircraft and DENTFARM were available. On 26, 29, November only lidar data was available at the time of preparation of this paper. The agreement between the lidar, the aircraft and DENTFARM observations is qualitatively good. No more can be expected since the air mass sampled by the three devices was not the same.

November 16, 1973--The lidar signals (Figs. 7A, B) show large, fluctuating signals from aerosols beginning at 0717, continuing to 1000. A denser layer occurs often near 275 m, corresponding approximately to a maximum in backscatter (bscat), condensation nuclei (CN) and temperature (T) observed by the MRI aircraft (Fig. 13), at a somewhat later hour ($\approx$ 1300 MST). Data from DENTFARM (Fig. 11) show a maximum in backscatter there at 1030. The maximum occurred in the lidar data (Fig. 7B) between 0823 and 1000, with large fluctuations. Rising wind at DENTFARM (Fig. 11) at 1200 was accompanied by decreasing particulate backscatter. The layers observed by the aircraft in the Henderson spiral (Fig. 13) appeared to persist in spite of the increased surface wind. No records of the wind aloft are available for this period and place. The lidar was not in operation after 1000.

November 21, 1973--In the early morning (0700-0800) Strong aerosol signals were observed, with denser layers at 75 to 100 m (Fig. 8). These occurred during a period of low wind velocity at DENTFARM (Fig. 12). Rising wind at DENTFARM, after 1000, was there accompanied by increasing backscatter, but at the lidar site cleaner air was observed. The aircraft data (Fig. 14) for the period ending 0915 shows large backscatter and CN from ground to 300 m; the lidar shows large backscatter generally below 250 m. The flight ending at 1234 (Fig. 15) shows much cleaner air, in agreement also with the lidar. This general agreement between the aircraft and lidar data cannot be extended to precise quantitative measures because of the different air masses and times of observation and because the lidar was not absolutely calibrated during this period. However, the aircraft data showed that size distribution did not vary greatly with altitude and thus, by the method outlined in the Appendix the lidar data can be used to estimate total loading if a single point calibration can be obtained from ground or air data. Presumably this data is available in other sections of this report.

November 26, 1973--The lidar signals (Figs. 9A, B) showed strong, variable, aerosol backscatter from 0944 to 1122. There was some evidence of an inversion near 300 m. Data from other observations was not available at the time of preparation of this paper.

November 29, 1973--Only weak and variable aerosol backscatter observed (Fig. 10) with no noteworthy features.

SUMMARY

The results of lidar observations of particulate air pollution at Adams County Fair Grounds have been reported. Other data, aircraft and ground, have been compared with the lidar data where available. Only on one day, 21 November, have the data been sufficiently concurrent and sufficiently contiguous to fully compare the aircraft and lidar data. Here the agreement is qualitatively good.

A method has been presented in the Appendix for estimating total particulate loading of the atmosphere up to the top range of the lidar (1115 m) under circumstances where the size-distribution and chemical composition were not greatly varying with height.

Especially valuable, but not analyzed in the text, is the insight, gained by lidar observations into the fluctuations of particulates. Great variation (compared with a mean) can be seen in Figs. 7-10. An analysis of such variations is required to arrive at proper spatial and temporal averaging procedures.

Additional data expected in other papers of this report may be further compared with the lidar data.

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APPENDIX

The presence of particulates in the atmosphere is detected by their properties when illuminated by light. Small particles scatter light in all directions (Mie scatter) in complicated patterns depending on the size, shape and composition of the particles and the wavelength of the light. Molecules of the atmosphere also scatter light (Rayleigh scatter), but effect is usually small compared with that due to particles in a polluted atmosphere. A portion of the light scattered directly back from the particles toward the source (laser) may be gathered by a telescope and detected. The power of the light detected is an approximate measure of the amount of particulate matter present. It is not exact, since the amount does not depend in a simple way on the number of particles nor on the mass of the particles. However, if the size distribution and chemical character remain approximately constant, the lidar signal is proportional to the number of particles present. Thus, if the mass density is known at the ground, its variation with height is proportional to the lidar signal, and the total amount up to the height recorded may be found by integrating under the lidar signal curve. Tables 2-5 give numerical values of the lidar signal (or radiance) from estimates which may be made quickly of the relative amounts of particulates in the beam. Adjustment must be made for the changing volume of the beam with range due to the 2 mr. The lidar signal received is proportional to the radiance of the particles in the source beam, which is proportional, under the circumstances cited above to the number of particles. The backscattered radiance is the radiant energy emitted toward the laser, by the particles, per unit time, per unit projected area of surface, per unit solid angle. Because, at the time of the experiments, no absolute calibration was available, the signal is presented in relative backscatter radiance units.

A laser is used as a source (instead of a searchlight) because its narrow beam width, monochromaticity and high peak pulse power permit detection of signals from great ranges even in daylight when the background skylight is a source of interfering noise. Because of those characteristics of the laser, the receiving telescope may be of limited field of view (excluding much skylight) and the detector may be protected by a narrow band optical filter centered at the laser wavelength. Pulse operation permits ranging just as in radar, and the high peak power permits high signal-to-noise ratios on a single pulse, simplifying signal processing. (The acronym LIDAR arose analogously to RADAR: Light Detection and Ranging.) Particles are regularly detected in the stratosphere at heights of 80 Km. However, for low lying pollution observation only the lower atmosphere is normally examined.

NUCLEATION CHARACTERISTICS OF DENVER AEROSOLS

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ABSTRACT

The aerosol physical parameters of Aitken, cloud, and ice nuclei concentrations, and of atmospheric light scattering are reported here for 16 days of measurements at two sites within the South Platte River Valley northeast of Denver, Colorado. These two sites are within the shallow basin that defines the urban area airflow patterns and represent locations fairly close to, and more removed from, the urban emission sources.

Measurements show that the atmospheric pollution at the more remote site is generally more dilute than at the closer site, but they consistently demonstrate that automobile traffic is the primary source of Aitken nuclei. Also consistently demonstrated is the conversion of Aitken nuclei to cloud nuclei and light scattering particles. This process proceeds slowly in the dark and is markedly accelerated in the sunlight. The striking increase of atmospheric ice nuclei from high winds is shown on two notable occasions. The measurements of ice nuclei from traffic or other urban sources are interpreted to show small increases in ice nuclei concentrations at both sites.

INTRODUCTION

The influence of cities, and particularly of automobile traffic, on atmospheric processes has been the subject of considerable research (e.g., Schaefer¹, Barrett et al.², Eldy et al.³, Weickmann⁴), and a definite relationship between man-made cloud and ice nuclei and precipitation effects has been demonstrated (e.g., Hobbs et al.⁵, Weickmann⁶).

In a long-range program of the Nucleation Chemistry Group, Atmospheric Physics and Chemistry Laboratory, ERL-NOAA, we had earlier conducted studies on the significance of the Denver urban aerosol (Pueschel et al.⁶); participation in the EPA-coordinated "Brown Cloud" experiment in November 1973 presented the opportunity to pursue this important subject further.

Aerosol parameters measured during the study period of 6-23 November 1973 were Aitken nuclei (AN), cloud condensation nuclei (CCN), and ice nuclei (IN) concentrations, and the atmospheric light scattering coefficient (b_{scat}). Chemical composition and surface characteristics of the Denver aerosol collected on 14 and 21 November 1973 have been reported (Van Valin et al.⁷), and these properties are not discussed here. AN, CCN, IN, and b_{scat} for those two days were also examined in detail; discussion of these parameters is included in the context of the examination of the entire study period.

By strict definition, AN are those particles that serve as condensation nuclei for the formation of droplets at the > 300 percent supersaturation achieved during the rapid adiabatic expansion produced in an Aitken nucleus counter; in common terminology, AN are all particles between molecular size and $0.2 \mu\text{m}$ diameter. In terms of number concentration in the atmosphere, AN are predominant. Most AN are smaller than the size required to produce appreciable light scattering. CCN are those particles that are suitable sites for the formation of water drops from condensation of water vapor in the natural atmosphere; they are necessarily wettable or soluble in water. Particles must be as large as or larger than a certain minimum size to be active as CCN at a given supersaturation, e.g., the minimum radius for wettable, but insoluble particles at 0.1 percent supersaturation is ca. $1.6 \mu\text{m}$, and at 1.0 percent it is ca. $0.13 \mu\text{m}$. The minimum radius for soluble particles is smaller by an order of magnitude or more. IN are those particles that serve as nuclei for the formation of ice crystals. IN are insoluble in water; their ice nucleating capability apparently depends upon the presence of surface sites that resemble the geometry of the ice crystal. Light scattering is accomplished by particles larger than $0.2 \mu\text{m}$ diameter. In the real atmosphere, essentially all light scattering is done by particles $0.2 < D < 2 \mu\text{m}$ because there are so few larger particles present.

EQUIPMENT AND LOCATION

AN concentrations were measured with the Environment-1 counter, b_{scat} with the Meteorology Research, Inc. nephelometer, CCN concentrations with the MBL thermal diffusion cloud chamber operating at 0.5% supersaturation, and IN concentrations with the NEAR counter. These instruments are mounted in a medium-size travel trailer, with the air sampling intakes at a height of 14 m above the ground.

From 5 November to 19 November 1973, our mobile laboratory was located at the Adams County Fairgrounds, 16 km northeast of the Denver city limits, and about 1.5 km west of the South Platte River. From 19 November to 23 November 1973 it was at the State of Colorado Humane Society about 6 km northeast of the Denver city limits and approximately 1 km east of the South Platte River. Both sites were within the river valley; the Fairgrounds and Humane Society sites were approximately 0.5 km from the west and east edges of the valley, respectively. According to Riehl and Crow⁸, the Denver urban plume is commonly carried northeast along the South Platte River valley during the night and early morning hours when light downslope winds occur along the eastern slope of the Front Range of the Rocky Mountains. During the daytime, when sufficient surface heating takes place, the direction of air flow reverses. Thus, one can imagine an oscillating flow of air within the valley, with urban pollutants being added at the southwest end of this system and removed and diluted toward the northeast.

OBSERVATIONS AND DISCUSSION

For the purpose of this report, we consider observations for the periods 6-17 and 20-23 November 1973. Figures 1 through 4 show AN, CCN, IN, b_{scat} , wind speed, and wind direction. To include enough time so that patterns are apparent, each figure covers four days. Wind speed and direction were taken from measurements of the EPA Mobile Field Laboratory at the Humane Society site, from the Welby monitoring site of the EPA Field Monitoring Program (Crow⁹), and from the National Weather Service-NOAA, Stapleton International Airport, in that order of preference. In addition, comments that we made in our project notebook have proved invaluable in the interpretation of our data in the light of local, on-site air movement, and in refreshing our memories.

Our notebook remarks for 6 November 1973 indicate a mostly cloudy sky, wind from the northeast at about 1.5 m sec^{-1} , and a distinctly visible pollution cloud to the northeast at 0730 MST. This weather situation continued, with alternately light northerly winds and calm air and visible pollution, until mid-afternoon when cloud cover decreased and visibility improved. The visual observation of an aged pollution cloud is corroborated by the AN, CCN, and b_{scat} measurements. AN continued to be supplied in rather high concentrations throughout the day from traffic on nearby roads; the greatest CCN concentration and b_{scat} occurred during mid-afternoon, when insolation had increased. In late afternoon and early evening the CN concentration and b_{scat} declined markedly.

On 7 November 1973 (Figure 1) the large increase of AN concentration coincided with the daily increase in traffic, although CCN and b_{scat} did not increase, probably because of cloudiness. The sky cleared about noon, but the accompanying increase in wind velocity was sufficient to dilute any possible atmospheric pollutants. A power outage interrupted our instrument operation from 1230 to 1430.

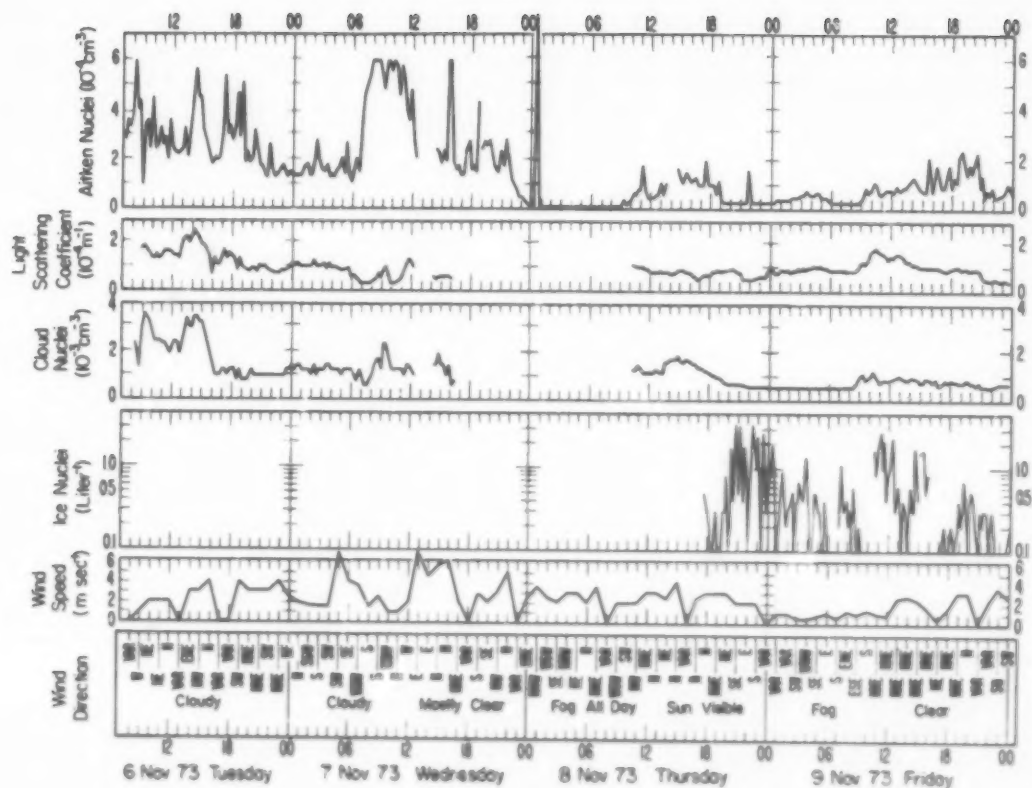


Figure 1 AN, CCN, and IN concentrations and b_{scat} as measured by the mobile laboratory at the Adams County Fairground site for 6-9 November 1973. Wind speed and direction were obtained from measurements of the EPA Mobile Field Laboratory, from the Welby Monitoring site of the EPA Field Monitoring Program, and from the National Weather Service.

Fog covered the site for the entire day of 8 November 1973 (Figure 1). The AN concentration did show a slight increase during the daylight hours, but, obviously, most particles were washed out by the fog. The apparent slight increases in CCN and b_{scat} are probably the result of instrument response to the fog, rather than to a solid aerosol.

Fog was also present on 9 November 1973 (Figure 1) until about noon, when the sky cleared. It is interesting to note that the AN concentration increased slightly as the fog (and relative humidity) decreased. The minor increase in b_{scat} at about 1100 is not readily explained, but it is obvious that the increasing numbers of AN were not appreciably converted to CCN and scattering particles, especially after sundown.

The variation of IN concentration between limits of approximately 0.4 and $1 \text{ } \mu\text{m}^{-1}$ appears to be related to wind direction, with the higher concentrations measured when the air movement was from the urban area. It is known (Morgan and Allee¹⁰) that engine operation using leaded gasoline produces many IN, but that typical polluted atmospheres deactivate the IN. The measurements shown here and those taken on subsequent days indicate, however equivocally, that the urban area is a minor source of IN.

The following day, Saturday, 10 November 1973, (Figure 2) was clear and warm, with the usual increase in AN corresponding to the daily increase in traffic. The lack of conversion to CCN and scattering particles may be explained by the linkage with synoptic airflow during mid-day (Crow⁹). This served to limit the AN source concentration during that time of the day when solar irradiation could have accelerated conversion.

Sunday, 11 November 1973, (Figure 2) was clear and warm, with air flow from the south southwest (urban area) until about 1000, when the wind direction shifted to northerly. The modest supply of AN from 1100 to 1400 came from the traffic east and north, but the source was too weak to produce measureable CCN and b_{scat} . After 1800 the wind shifted to southerly and moved an aged pollution plume across the site. This was dispelled when another wind shift occurred about 0200 on 12 November.

During the morning of 12 November 1973 (Figure 2), there were blustery west winds closer to the mountains west of the site, but within the valley pollution was visible. Monday morning traffic produced an ample supply of AN, but the lack of direct sunlight retarded conversion to CCN and scattering sized particles, and the comparatively high wind velocities served to dilute the air mass before significant non-irradiated processes could take place. During this time the comparatively high IN concentration may have been produced partly by wind-raised dust. A lessening of wind velocities and a shift in direction to southwesterly in the early evening permitted the city plume to be carried to the site.

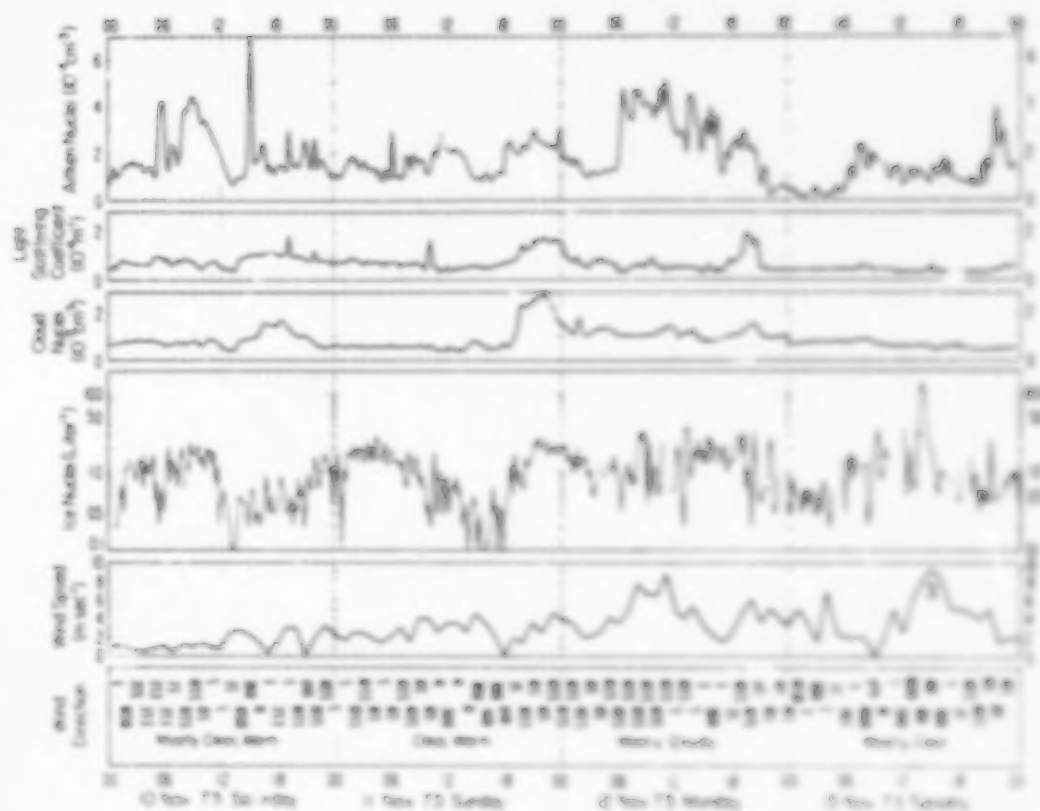


Figure 2 Parameters (see Figure 1) for 10-13 November 1971, Adams County Fairground site. The notation "G11" in the wind speed record shows the peak gust velocity during the indicated hour.

On 13 November 1973 (Figure 2), a modest increase in AN corresponded to the daily traffic increase, but the changeable and sometimes blustery winds continually diluted the valley air. At 1400 the first example was seen during this study of the effects of high wind on the IN concentration. This order-of-magnitude IN increase is from wind-raised dust; we estimated gust velocities to be as much as 15 m sec^{-1} at the site at 1330.

The observations of 14 November (Figure 3) have been examined and reported in detail (Van Valin et al.⁷), but the essential factors are as follows: The maximum CCN, AN, and b_{scat} occurred only about 1.5 h after sunrise. Photolytic aerosol production was therefore not a factor; CCN and b_{scat} increases were from normal coagulation and reaction processes taking place in the urban plume as it was carried northeastward from the city. The sudden onset of the high-velocity "chinook" winds just before 1100 swept away the man-made pollution. AN, CCN, and b_{scat} abruptly dropped to very low levels, but the IN concentration just as quickly increased by nearly two orders of magnitude. This is a vivid example of natural aerosol production that was merely hinted at in the brief episode of the previous day.

The expected AN increase appeared, coincident with traffic, on 15 November (Figure 3) and was accompanied, after a minor time lag, by a small increase in b_{scat} . Unfortunately, our CCN and IN instruments were out of operation for all or part of this and the succeeding two days. However, during most of this study period we noted a fair correlation between CCN concentration and b_{scat} , and we feel justified in assuming a similar minor increase in CCN, followed by a return to low concentrations after about 1100. The sky was mostly cloudy all day, preventing the sunlight-accelerated particle production, and the fairly vigorous wind flow was from the southeast, preventing most of the urban plume from reaching the site.

The 16th and 17th of November (Figure 3) were mostly cloudy, with the more-or-less expected AN supply. At 1000 on 16 November a minor pollution concentration was visible west of the site, but the easterly winds supplied fresh air and during the day no pollution build-up was measured. At about 1900 the wind became southwesterly, with lower velocity, and the urban plume was carried across our sampling site; the maximum concentration, according to b_{scat} , was at 0300 on 17 November.

On 19 November we moved our mobile laboratory to the Humane Society site, next to the EPA mobile field laboratory. A snowfall began during the afternoon, continued through the night, and ended the following morning. No observations worth reporting were made until late afternoon of the 20th (Figure 4), when a modest increase in CCN and b_{scat} indicated the presence of the urban plume.

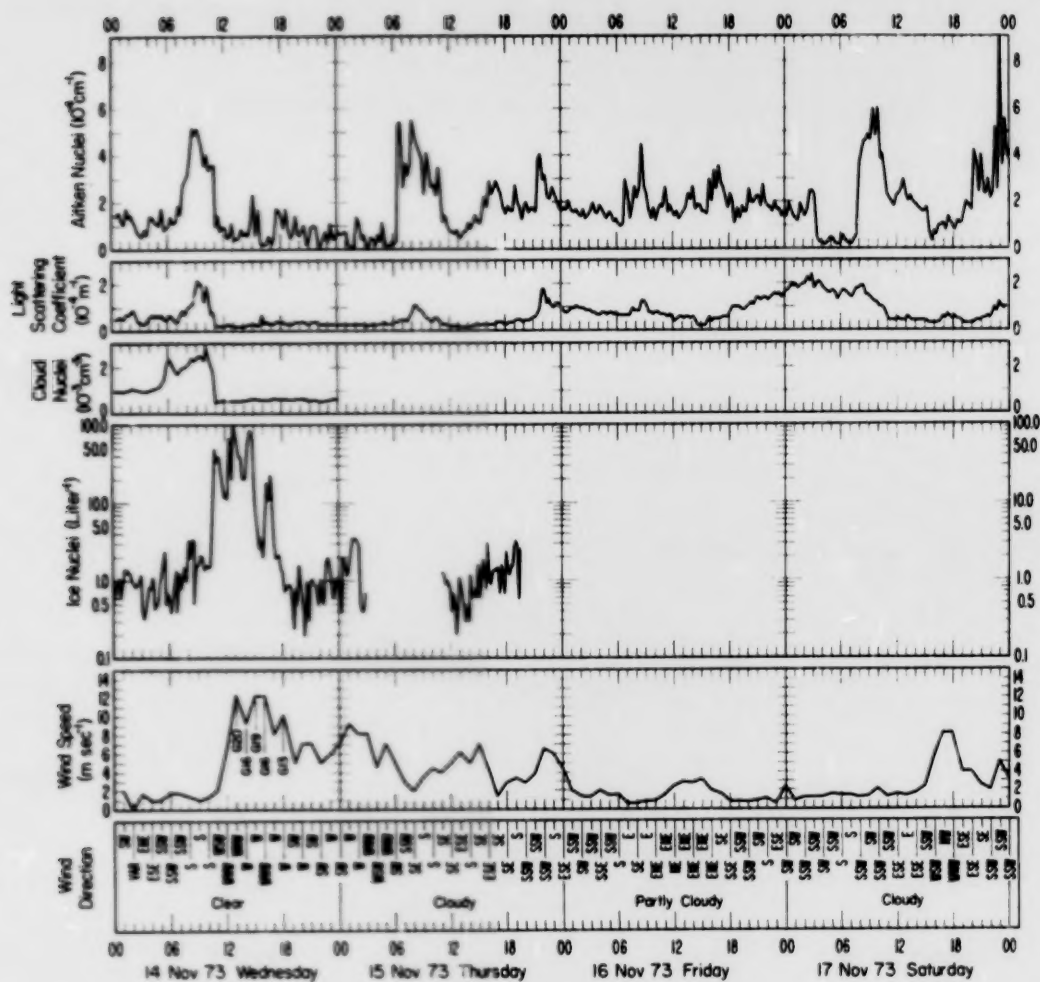


Figure 3 Parameters (see Figure 1) for 14-17 November 1973, Adams County Fairground site. Peak gust velocities are noted in the wind speed record.

The observations of 21 November (Figure 4) have been analyzed in detail and reported (Van Valin et al.⁷), but a summary is given here. A heavy fog from 0400 to 0540 produced elevations in b_{scat} and the apparent CCN concentration, but pollution-produced increases in these parameters and in AN coincided with the morning traffic increase. Solar irradiation accelerated the conversion, which resulted in a relative decrease in the AN concentration. At about 1200, the wind shifted to the east and a cloud cover moved in. The CCN and b_{scat} immediately decreased to essentially "clean air" levels, whereas the AN concentration continued at fairly high levels, varying only in response to the varying rate of dilution by the east wind. The important role of sunlight is illustrated here. Because of the location just west and northwest of heavily traveled roads we would have expected some increase in CCN and b_{scat} if the sun had been shining. We believe that the indicated increase, during the pollution episode, of the IN concentration was real and is an indication that engine-produced IN were not completely deactivated before reaching the site; nearly complete deactivation seemed to be the case at the more remote Fairgrounds site.

Beginning at about 0200 on 22 November (Thanksgiving Day) (Figure 4), the city plume was carried across the site, but traffic was very light during the day and the easterly winds around midday supplied clean air. A tripped circuit breaker dropped our CCN counter off the line, but there is no reason to believe that CCN measurements would have contradicted the b_{scat} measurements. Late in the evening a southwest wind carried an aged aerosol cloud across the site. The density of this pollution cloud decreased in the early morning hours of November 23 (Figure 4) and then was somewhat replenished as the morning workday traffic began. At about 1000 the wind shifted to southeasterly and became stronger, but under the influence of sunlight the b_{scat} declined only gradually. This observation further supports our previously stated thesis (Pueschel et al.⁶) that sunlight is a powerful factor in the creation of CCN and light scattering particles.

In Figure 5 we show an aerosol size distribution for membrane filter samples collected on 21 November at the Humane Society site. This was done by a replicating technique with the transmission electron microscope. The dashed line represents six samples collected from 0610 until 0830; the solid line represents four samples collected from 0900 until 1126. The aerosol populations are the same at the lower end of the size distribution, but in the particle size range from $0.08 \mu\text{m}$ to $0.25 \mu\text{m}$ the particle concentrations are significantly different and show the impact of automobile traffic. There were too few particles larger than $0.7 \mu\text{m}$ to form a statistically significant sample.

The ability of particles to serve as CCN depends upon both particle size and chemistry; at supersaturations of less than 0.5 percent, such as are found in nature, water insoluble particles of diameter less than approximately $0.6 \mu\text{m}$ will not be active as CCN (Pueschel and Weickmann¹¹). It is apparent, therefore, that either particle solubilization or particle growth must take place before the automobile engine-derived particles can enter into the liquid water nucleation picture.

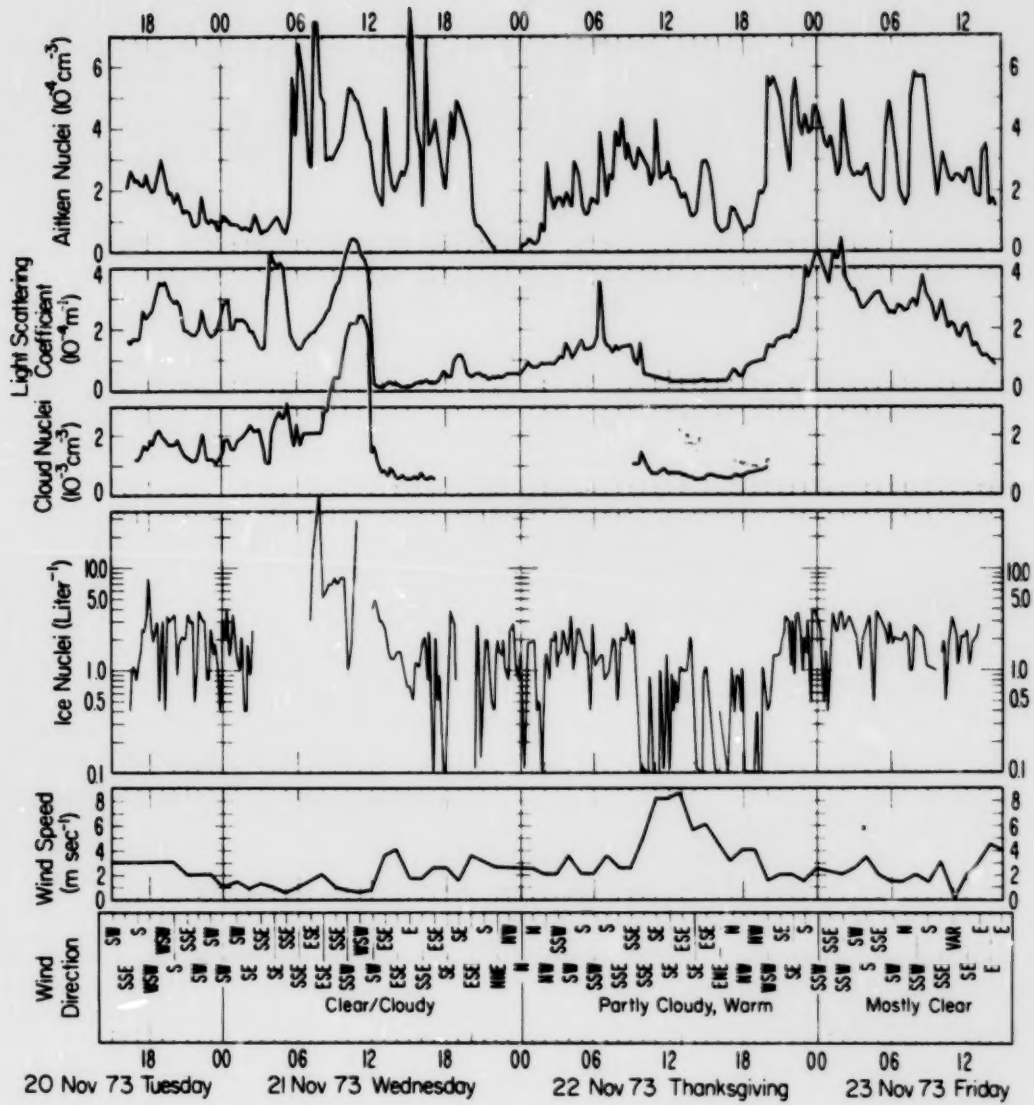


Figure 4 Parameters (see Figure 1) for 20-23 November 1973, Humane society site.

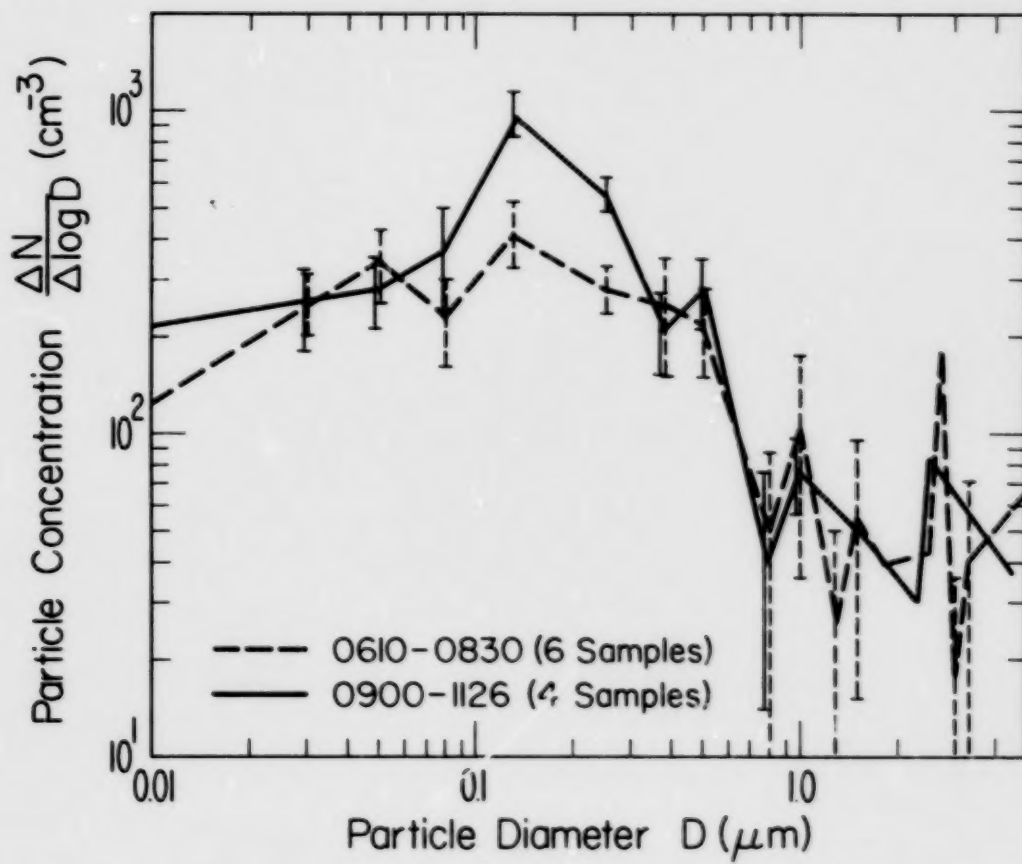


Figure 5 Aerosol size distribution at the Humane Society site on 21 November 1973.

CONCLUSIONS

Examination of the aerosol parameters measured during this study in the vicinity of Denver leads to the following points:

- . AN are produced primarily by automobile traffic.
- . AN are converted by coagulation and chemical reaction to CCN and particles of light scattering size.
- . This conversion of AN to CCN and light scattering particles occurs slowly in the dark and much faster in the sunlight.
- . Although it has been shown that operation of engines on leaded gasoline produces large numbers of IN, most IN are deactivated in the polluted atmosphere.
- . Automobile traffic in Denver constitutes a low-level source of IN.
- . Natural pollution in the form of dust raised during high winds introduces orders-of-magnitude more IN to the atmosphere than do Denver area emissions.

ACKNOWLEDGMENTS

We take this opportunity to thank Richard A. Proulx for his part in this study. His willingness to work early and late, and his effectiveness at all times were important and at times decisive factors in the success of the project.

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ATMOSPHERIC AEROSOL DYNAMICS: THE DENVER BROWN CLOUD

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ABSTRACT

Pollution conditions which arise in the Denver area are studied using a numerical model for the evolution of the aerosol size distribution. The time variation of the particle size distribution, total particle number, total particle mass and light scattering coefficient provide valuable insight into the mechanisms of particle growth and the color of the "brown cloud."

INTRODUCTION

In order to propose rational control policies for the Denver "brown cloud," a knowledge of the dynamics and relative importance of the various pollutants is required. To aid in the interpretation of the field study data on particulate matter for such "episode" conditions, we have developed a computer model for the evolution of the Denver aerosol. Although the model represents a gross simplification of typical Denver "episode" conditions, it does provide valuable insight into the dynamics and produces several useful predictions about the mechanisms of particle growth and the color of the "brown cloud." Details of the model and analysis of the results follow.

DYNAMIC MODEL

The dynamic model includes advective and (implicitly) convective flows, meteorological conditions, and aerosol processes assumed to be operating during a typical "winter episode" in Denver. Basically, the evolution of the particle size distribution in a parcel of air traversing the city is considered. The parcel itself is bounded by the ground and the top of the mixing layer. Initially the parcel contains a distribution of particles. As a parcel moves across the city the aerosols within the parcel evolve according to a number of mechanisms.

The description of air movement is highly simplified. "Heat island effects," the "chimney effect" and complex air flows such as horizontal dispersion and advection other than drainage flows are neglected. The assumption of relatively small mixing heights and

cyclical drainage flows is supported by several previous meteorological studies^{1,2}. The evolution of aerosol itself depends upon coagulation, dry deposition, primary source input, condensation (as a function of ozone concentrations), vertical mixing, and the advective drainage flows associated with the Platte River Valley. This basic model is schematically depicted in Figure 1.

The mathematical expressions which describe the various processes are only outlined in this paper since complete derivations are available in the literature^{3,4,5}. First we present the general equation for the evolution of the particle size density and then we discuss each growth term separately. The parameters particularly relevant to the Denver aerosol are noted.

We believe that all current evidence, to be discussed below, supports the view that the Denver aerosol during winter episode conditions, is dominated by primary sources. A very accurate description of the dynamics of such an aerosol is afforded by the evolution equation for the particle number density function. The following relation is assumed to describe the evolution of the density function $n(x, \vec{r}, t)$ for an aerosol with convective transport^{5,7}:

$$\begin{aligned} \frac{\partial n}{\partial t}(x, \vec{r}, t) + \nabla \cdot \vec{V} n(x, \vec{r}, t) = & \nabla \cdot \vec{K} \cdot \nabla n(x, \vec{r}, t) \\ & + 1/2 \int_0^x dx' b(x-x', x') n(x-x', \vec{r}, t) n(x', \vec{r}, t) \\ & - n(x, \vec{r}, t) \int_0^\infty dx' b(x', x) n(x', \vec{r}, t) \\ & - \frac{\partial}{\partial x} \psi(x) n(x, \vec{r}, t) + \frac{\partial^2}{\partial x^2} \alpha(x) n(x, \vec{r}, t) \\ & + \vec{G}(x) \cdot \nabla n(x, \vec{r}, t) + \sum_p \dot{V}_p(x, \vec{r}, t) + \sum_j \dot{V}_{N_j}(x, \vec{r}, t) \end{aligned} \quad (1)$$

where $n(x, \vec{r}, t)$ is the number of aerosol particles having mass, x , in the range x , dx at point $\vec{r}$ in space at time t . $\vec{V}$ is the fluid velocity. The first term on the right hand side of this equation accounts for the turbulent dispersion of particles, where $\vec{K}$ is the eddy diffusivity tensor. The second and third terms on the right hand side of the equation represent the change in $n(x, \vec{r}, t)$ due to coagulation^{3,4,5}. The

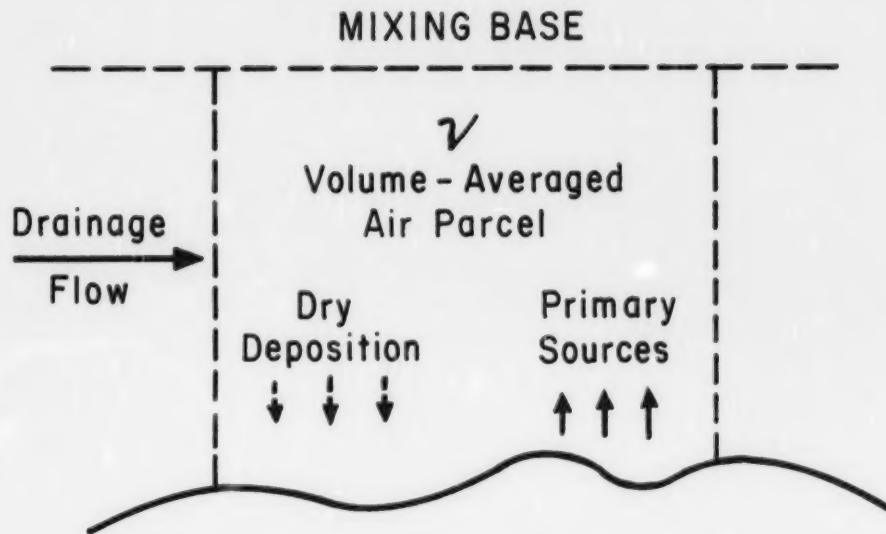


FIG. 1: SCHEMATIC DIAGRAM OF MODEL

fourth and fifth terms describe the change in $n(x, \vec{r}, t)$ owing to condensation of trace gaseous substances. In the next term $\vec{G}(x)$ is the sedimentation velocity of a particle of mass x . $\dot{V}(x, \vec{r}, t)$ represents the rate of production of particles of mass x at $\vec{r}, t$ from primary sources. $\dot{V}_N(x, \vec{r}, t)$ is the rate of production of particles of mass x at $\vec{r}, t$ by homogeneous nucleation of the j -th chemical species. It should be noted that heterogeneous nucleation of condensable species is accounted for by the condensation terms, four and five. The form of the coagulation coefficient $b(x, x')$, the condensation coefficients $\psi(x), \alpha(x)$, and the details of the other terms are discussed below.

Equation 1 is, of course, for the general case of an aerosol in the atmosphere, or any fluid in general motion, coupled to the energy and momentum balance equations. It is, of course, also coupled closely to the continuity equations for the various chemical species undergoing homogeneous nucleation and condensation with the aerosol phase³. For any turbulent fluid, equation 1 is not in a useful form. By analogy with the usual procedure for turbulent dispersion of non-reactive gases these quantities can be expressed in terms of time averaged quantities. Subsequent to this time averaging, we carry out a volume averaging procedure, where the volume average of the density function is defined as

$$\langle n(x) \rangle = \frac{1}{V} \int n(x, \vec{r}, t) d\vec{r}. \quad (2)$$

where for brevity $\langle n(x) \rangle$ is written for $\langle n(x, t) \rangle$. The control volume V may be thought of as the volume of a "box" whose vertical bounds are determined by the ground and the top of the mixing layer. The box covers a surface area of 5.3 km^2 which is set by the estimate of the average wind speed (see below).

Through this volume averaging procedure we will, in effect, follow the evolution of the particle size distribution in a particular control volume as it moves across the city. This model, obviously, involves gross simplifications in that the pollutants in the box are assumed to be well mixed from ground to the mixing height and diffusion out of the box is not considered. In particular, a moving control volume was chosen in order to study explicitly the evolution of the aerosol in the cyclical drainage flows associated with winter episode conditions in Denver. A more comprehensive and conventional model could be constructed through the use of a multiple box model in a fixed matrix over Denver and its environs.

Unfortunately, we had insufficient information for Denver to permit such calculations. Information is now being acquired and it is our purpose to carry out more detailed analyses. In this paper we carry out the calculation described above for a single control volume which represents an average for the entire city.

Following through with our present development, the volume average of equation (1) is taken according to equation (2). If the resultant volume integrals are converted where applicable to surface integrals, an evolution for $\langle n(x) \rangle$ is obtained having the form:

$$\begin{aligned} \frac{\partial \langle n(x) \rangle}{\partial t} = & (1/2) \int_0^x b(x-x', x') \langle n(x-x') \rangle \langle n(x') \rangle dx' \quad (3) \\ & - \langle n(x) \rangle \int_0^\infty b(x, x') \langle n(x') \rangle dx' \\ & + \frac{\partial^2}{\partial x^2} \langle \alpha(x) \rangle \langle n(x) \rangle - \frac{\partial}{\partial x} \langle \psi(x) \rangle \langle n(x) \rangle \\ & - \langle \sigma(x) \rangle \langle n(x) \rangle + \sum_p \tau_i W_i(x) \end{aligned}$$

For daytime conditions the volume averaged density $\langle n(x) \rangle$ is representative of $n(x, \vec{r}, t)$ throughout the mixed layer. However, at night there may be a substantial vertical variation in $n(x, \vec{r}, t)$, and therefore the meaning of $\langle n(x) \rangle$ may become less precise.

Several other changes between equation (1) and equation (3) should be noted. The volume averaging procedure introduces explicitly the unspecified boundary conditions of equation (1) into equation (3). For the system under discussion, these boundary conditions appear in equation (3) as the term $\langle \sigma(x) \rangle \langle n(x) \rangle$ which represents those processes effecting removal of particles from the control volume, v . Homogeneous nucleation is neglected since the time scale over which the nucleation rate might be significant is small compared to the time scales of the other rate processes. The last term on the right hand side of equation (3) represents the volume average of the rate of production of particles from primary sources and the summation extends over all primary sources, i , $\langle \alpha(x) \rangle$, $\langle \psi(x) \rangle$, and $\sigma(x)$ are explicitly functions of time; τ_i depends implicitly on time as will be indicated below.

COAGULATION

For the coagulation coefficient $b(x, x')$ we assume the particles are interacting by Brownian coagulation only. Given this assumption, $b(x, x')$ becomes ^{3,4}.

$$b(x', x) = 4\pi(R + R') (\Delta + \Delta')\sigma \quad (4)$$

$$x = 4/3\pi R^3 \rho$$

$$u = (8kT/\pi x)^{1/2}$$

$$\Delta = (kT/6\pi\mu R) \left\{ 1 + \frac{\Omega}{R} (A + B^{-CR/\Omega}) \right\}$$

$$\sigma = 1/[1 + 4(\Delta + \Delta')/(R + R') (u^2 + u'^2)^{1/2}]$$

where ρ is the particle mass density, μ and Ω are respectively the viscosity and mean free path of the gas and A, B, C are the constants in Millikan's empirical equation for particle mobility³. R, Δ , and u are respectively the radius, diffusion coefficient and mean thermal speed of a particle. kT is the thermal energy. Compared to other coagulation mechanisms, Brownian coagulation appears to be dominant for the Denver aerosol. This feature will receive future study in our laboratory.

CONDENSATION

In equation (3) condensation is represented by two terms,

$\frac{\partial^2}{\partial x^2} (\langle \alpha(x) \rangle \langle n(x) \rangle) - \frac{\partial}{\partial x} (\langle \psi(x) \rangle \langle n(x) \rangle)$. For the purpose of this paper, the first term which describes the dispersion of the particle size distribution is neglected. Furthermore, the second term only accounts for the diffusional transfer of chemical species to the surface of a particle. Motivation for these assumptions is discussed elsewhere.⁷ By definition $\langle \psi(x) \rangle$ has the form:

$$\langle \psi(x) \rangle = \frac{1.21u_j(S_j - S_{jo} e^{Kx^{-1/3}})x^{2/3}}{1 + 0.28(e^{-1.4(10^5)x^{1/3}} - 1) + 5.43(10^4)x^{1/3}} \quad (5)$$

where S_{j0} is the mass concentration of component j corresponding to the vapor pressure of j over a plane liquid (or solid) surface. u_j is the mean thermal speed of molecule j . K is the Kelvin coefficient appropriate for the condensing substance associated with the Kelvin effect:

$$K = 2\gamma V_{JL}/kT \quad (6)$$

where γ is the surface tension at a particle-gas interface and V_{JL} is the volume of a vapor molecule of j in the liquid (solid) phase. S_j is the mass concentration of the j^{th} chemical species.

Since the conversion of H_2SO_4 aerosol is assumed to be the only significant mechanism for secondary source input, we need to consider only one chemical species. Given this assumption the mass concentration S_j can be calculated from the concentrations of ozone, olefin, and sulfur dioxide and from the known mass conversion rate of H_2SO_4 in the following way. The mass conversion is just the rate of change of particle mass due to condensation, dM_c/dt :

$$\frac{\partial M_c}{\partial t} = \int_0^x \langle n(x) \rangle \langle \psi(x) \rangle dx \quad (7)$$

Given the concentrations of olefin, ozone and sulfur dioxide during an episode day in Denver⁸, the volume conversion is deduced from experimental results relating the H_2SO_4 conversion rate to the chemical concentrations⁹. The concentration of olefin is assumed to be 8.2 ppm and the concentration of sulfur dioxide is .066 ppm⁸. These values remain constant throughout the calculations since the diurnal variation of these substances is not significant. The ozone concentration, $[O_3]$, however, varies in time by the following perscription:

$$[O_3] = .0025, \quad t=0 - 600 \text{ and } 1800-2400 \text{ hours} \quad (8)$$

$$[O_3] = .0025 \text{ ppm} + (.09 \text{ ppm} - .0025 \text{ ppm}) \sin\left(\frac{\pi}{2} \left(\frac{t-600}{800}\right)\right), \quad t=600-1400 \text{ hours}$$

$$[O_3] = .0025 \text{ ppm} + (.09 \text{ ppm} - .0025 \text{ ppm}) \sin\left(\frac{\pi}{2} \left(\frac{t-1400}{400}\right)\right), \quad t=1400-1800 \text{ hours}$$

This model for the diurnal variation is illustrated in Figure 2.

DEPOSITION

The deposition coefficient, $\langle \sigma(x) \rangle$, is expressed as

$$\langle \sigma(x) \rangle = V(x,t)/H(t) \quad (9)$$

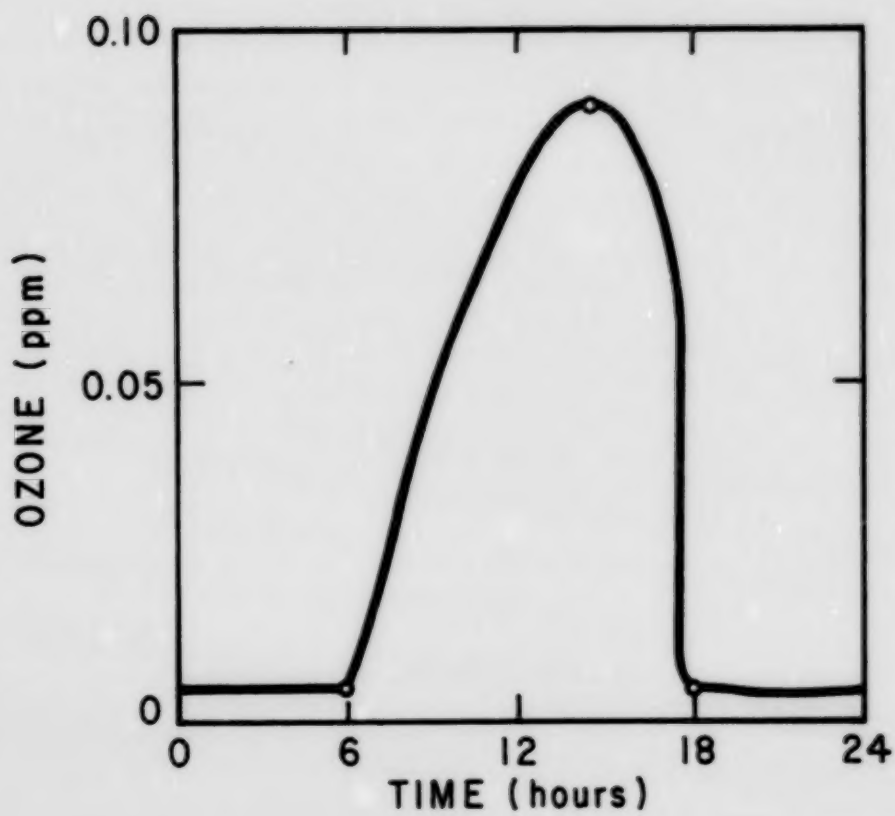


FIG. 2: DIURNAL VARIATION OF OZONE

where $H(t)$ is the mixing height (to be discussed later) and $V(x,t)$ is the deposition velocity:

$$V(x,t) = v(x,t) + V_0(x). \quad (10)$$

$V_0(x)$, the gravitational settling velocity, is given by:

$$V_0(x) = \frac{4}{3} \pi R^3 \rho / 6 \pi \mu R \quad (11)$$

where g is the acceleration of gravity, ρ is the particle density and μ is the viscosity of air. The density of quartz (a principal constituent of the large particle mode) is taken in this calculation as the particle density. $V_0(x)$ is constant in time but $v(x,t)$ varies as

$$v(x,t) = U(x) L(t). \quad (12)$$

$U(x)$ is fit to the sedimentation velocity estimated by Sehmel¹⁰ for a friction speed, U_* , of 20 cm/sec and a surface roughness of 10.0 cm. Sehmel's velocity estimates are illustrated in Figure 3. When $U_* = 0$, of course, the only operant removal mechanism is gravitational sedimentation. The dynamics of the aerosol is very sensitive to the choice of this deposition velocity. The values used in this simulation were arrived at by trial and error and represent a best, but not necessarily unique, choice. The relationship of $v(x,t)$ and wind speed is taken into account by the time factor $L(t)$ --a monitor⁸ of the diurnal variation of wind speed for a typical Denver "episode". $L(t)$, illustrated in Figure 4, varies in the following way:

$$L(t) = 0.35 \cos \left(\frac{\pi}{2} \left(\frac{t-0}{400} \right) \right) + 0.15, \quad t = 0-400 \text{ hours} \quad (13)$$

$$L(t) = 0.85 \sin \left(\frac{\pi}{2} \left(\frac{t-400}{1000} \right) \right) + 0.15, \quad t = 400-1400 \text{ hours}$$

$$L(t) = 0.65 \cos \left(\frac{\pi}{2} \left(\frac{t-1400}{600} \right) \right) + 0.35, \quad t = 1400-2000 \text{ hours}$$

$$L(t) = 0.15 \sin \left(\frac{\pi}{2} \left(\frac{t-2000}{400} \right) \right) + 0.35, \quad t = 2000-2400 \text{ hours}$$

In the volume average context, the deposition process at the surface is converted into an effective volumetric sink term. Hence, during night-time meteorological conditions, some imprecision is introduced through this procedure.

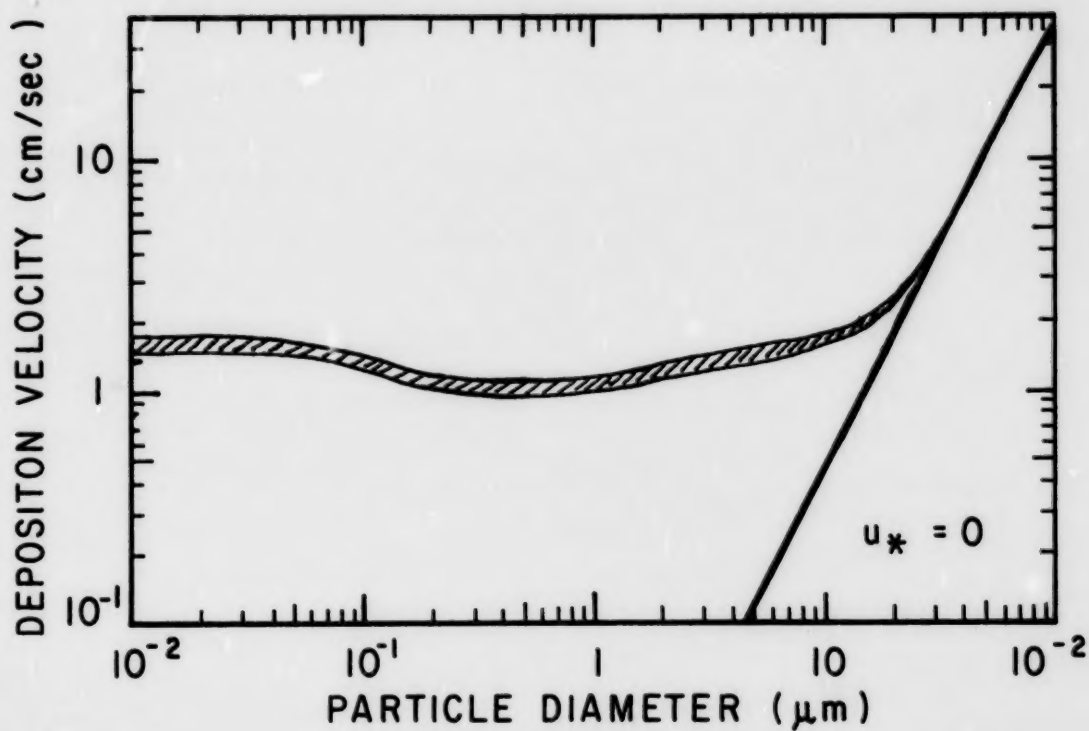


FIG. 3: DEPOSITION VELOCITY AS A FUNCTION
OF PARTICLE SIZE

FRICTION VELOCITY = 20 CM/SEC.
ROUGHNESS HEIGHT = 10 CM.

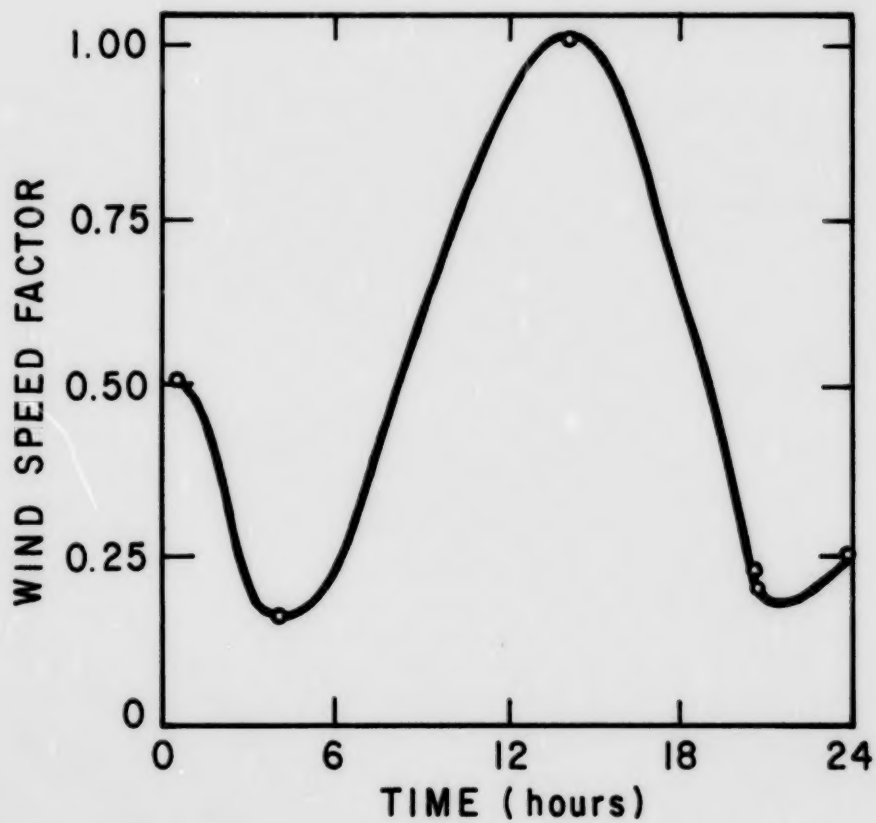


FIG. 4: DIURNAL VARIATION OF WIND SPEED FACTOR

PRIMARY SOURCES

The primary source term is the sum of all the source contributions:

$$\sum_p \tau_i W_i(x) = \frac{F(t)}{H(t)} \sum_{i=1}^5 \frac{A_i}{\ln \beta_i \sqrt{2\pi}} \frac{1}{x} \exp \left(-(\ln x - \ln \bar{x}_i)^2 / 2(\ln \beta_i)^2 \right) \quad (14)$$

$F(t)$ is the valley flow factor which accounts for advection and $H(t)$ is the mixing height. Since no information on source size distributions is available, each of the five sources are assumed to be lognormal distributions in mass. The magnitudes A_i are calculated from emission inventories for Denver, I_i , in the following manner. For a lognormal distribution the first moment, which is the total mass emission flux, I_i , is given by,

$$I_i = A_i \exp \left(\ln \bar{x}_i + 1/2 \ln \beta_i^2 \right). \quad (15)$$

The sources and their emission fluxes, I_i , are listed in Table 1. These rates were calculated from the reported tons per year values given by the PEDCO study¹¹. In Table 2 are listed the particle diameters $\bar{D}_i$ corresponding to the mean mass and the variance, $(\ln \beta_i)^2$, of the lognormal distributions of the primary sources. Size distribution data for industrial sources were obtained from a report by Shannon and German¹². The data for dust were calculated from a paper by Schutz and Jaenicke¹³. Transportation is taken from an estimate of residence times in an exhaust system⁵. Each source magnitude A_i is constant over a one hour period, but varies from hour to hour. This time dependence of sources reflects the diurnal change in emission rates. As illustrated in Figure 5, the point sources and fuel combustion are constant whereas traffic dust and traffic exhaust have maxima during rush hours. Construction dust is a constant during working hours and zero otherwise.

VERTICAL MIXING

Vertical mixing is accounted for by the time variation in mixing height $H(t)$ and volume correction to the density. The time variation in mixing height for a typical episode day¹⁴, illustrated in Figure 6, is given as:

Table 1. ESTIMATED EMISSION RATES FOR PRIMARY PARTICULATE SOURCES

<u>Sources</u>	<u>I_i, Eq. 15</u>	
	<u>Emission Flux</u>	<u>Fraction of Total</u>
	<u>24 hr. Average</u>	
	<u>g/km²sec</u>	
1. Traffic dust (unpaved roads, sand and salt on roads)	0.815	0.428
2. Construction dust	0.23	0.12
3. Point sources	0.14	0.075
4. Fuel combustion + process losses + solid waste disposal	0.18	0.095
5. Transportation	0.34	0.18
TOTAL	1.90	1.00

Table 2. SIZE DISTRIBUTION PARAMETERS FOR PRIMARY PARTICULATE SOURCES

<u>Source</u>	<u>Particle Diameter</u>	
	<u>D_i (μm)</u>	<u>β_i, Eq. 14</u>
1. Traffic dust	5	5
2. Construction dust	5	5
3. Point sources	.2	2.5
4. Fuel Combustion + process losses + solid waste disposal	.2	2.5
5. Transportation	.10	2

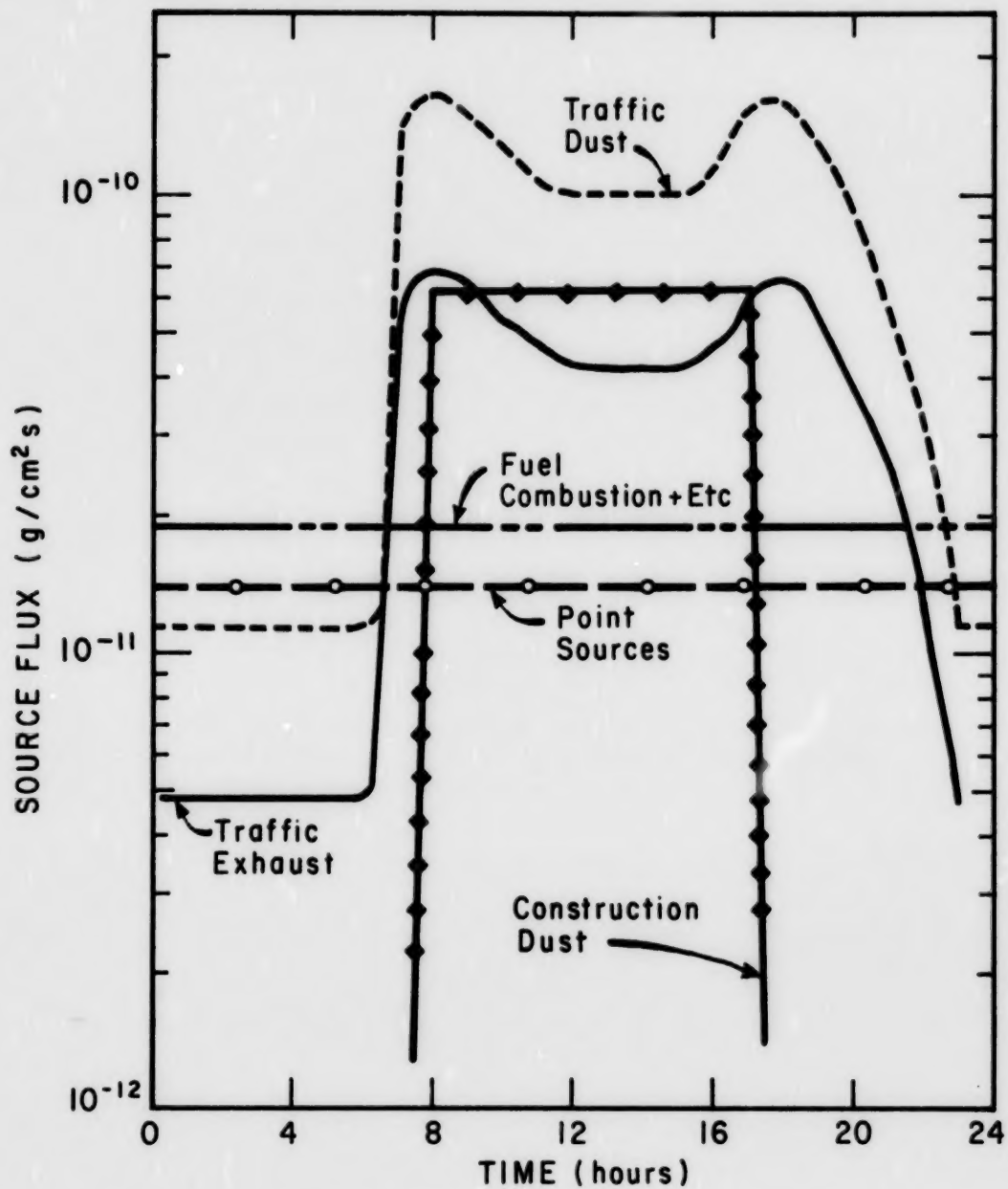


FIG. 5: DIURNAL VARIATION OF PRIMARY PARTICULATE SOURCES

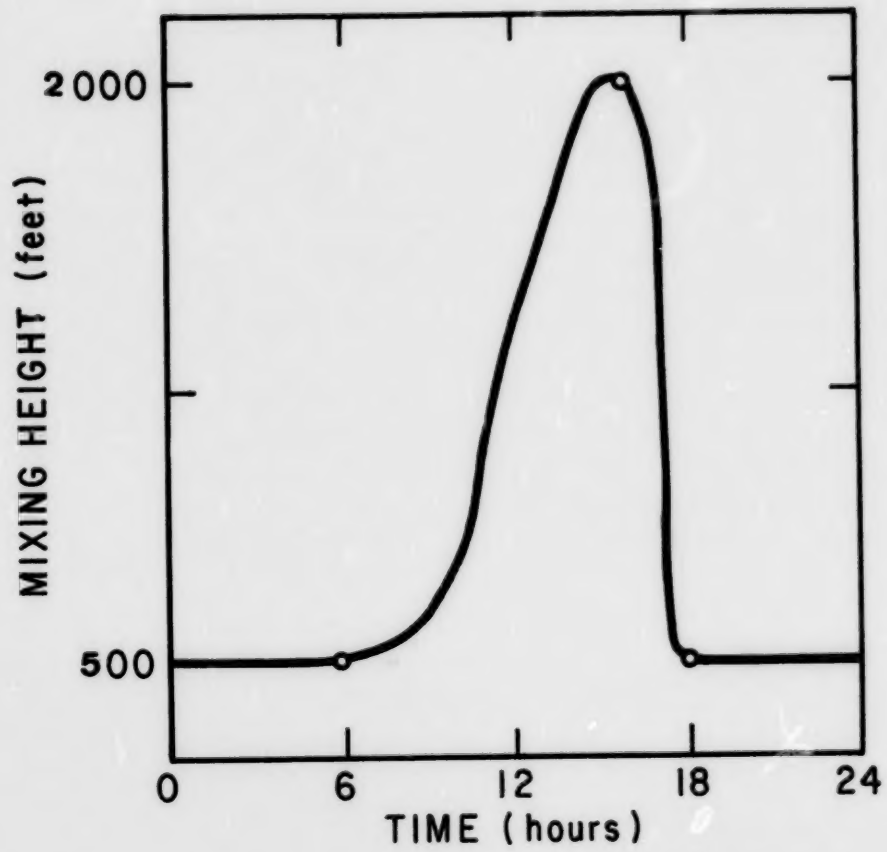


FIG. 6: DIURNAL VARIATION OF MIXING HEIGHT

$$H(t) = 200 \text{ meters, } t = 0-600 \text{ and } 1800-2400 \text{ hours} \quad (16)$$

$$H(t) = 200 \text{ meters} + 500 \text{ meters} \sin \left(\frac{\pi}{2} \left(\frac{t-600}{800} \right) \right), t=600-1400 \text{ hours}$$

$$H(t) = 500 \text{ feet} + 1500 \text{ feet} \cos \left(\frac{\pi}{2} \left(\frac{t-1400}{400} \right) \right), t=1400-1800 \text{ hours}.$$

When the mixing height changes, the volume of the region over which the density is averaged changes. As a mixing height increases the density decreases assuming there is no substantial particulate concentration above the mixing height as it rises. As the mixing height decreases, the density increases due to the convection but also decreases due to the loss of particles above the mixing height. The density corrected for the increase of mixing height is

$$n_{t + \Delta t}^{(1)} = \frac{H}{H + \Delta H} n_t^{(1)} \quad (17)$$

and the density corrected for the decrease of mixing height is (at the appropriate time step)

$$n_{t + \Delta t}^{(1)} = \frac{H}{H - \Delta H} n_t^{(1)}. \quad (18)$$

These modifications are illustrated in Figure 7.

ADVECTION

The advective drainage flows are taken into account by the valley flow factor $F(t)$ in the source term. A background source input is always assumed. However, as the air parcel moves out of the city the source input decreases. When the air parcel is over the city the sources are full strength. Figure 8 illustrates the diurnal variation of $F(t)$. We chose an air parcel which was north of the city at midnight, moved south until the afternoon and then reversed its flow and drained down the valley in the late afternoon and evening. Assuming an average wind speed of 0.9 meters per second, the air parcel would complete the cycle of moving up and down the valley in one day.

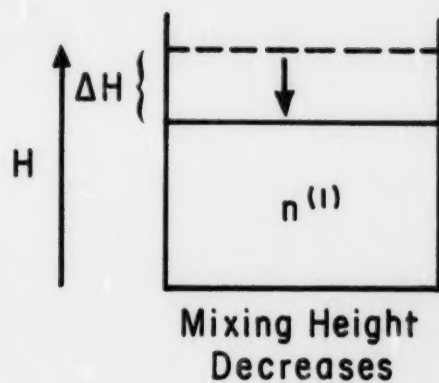
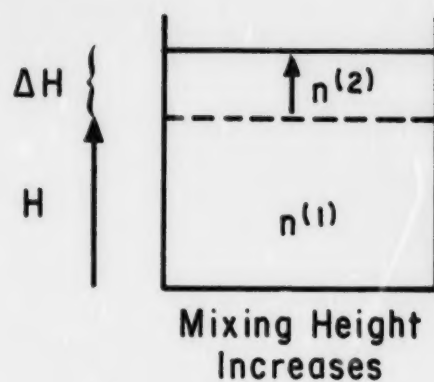


FIG. 7: VOLUME CORRECTION TO
PARTICULATE NUMBER DENSITY

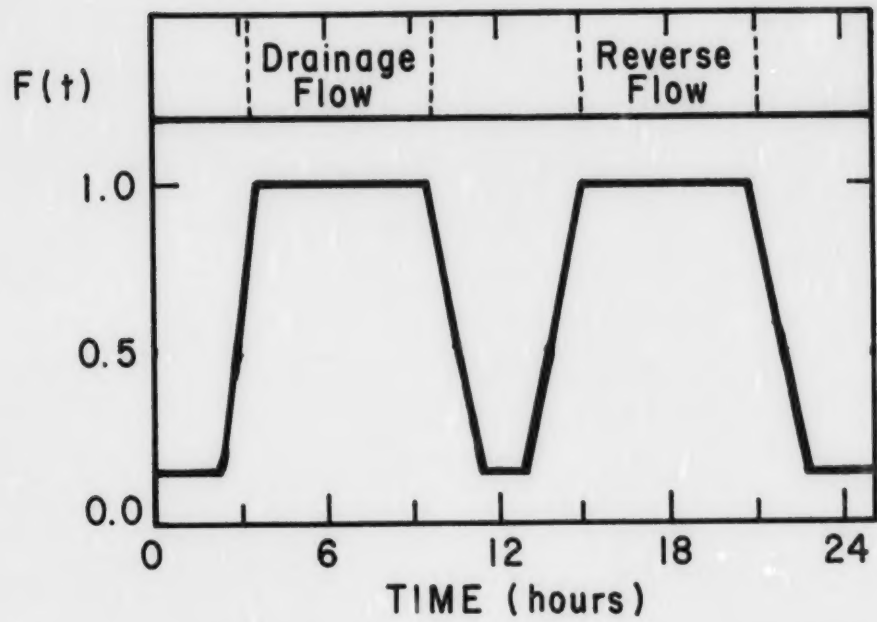


FIG. 8: DIURNAL VARIATION OF VALLEY FLOW FACTOR

INITIAL SIZE DISTRIBUTION

For the initial size distribution we assumed a typical nighttime aerosol distribution¹⁵. The distribution is expressed as the sum of two lognormal functions:

$$\begin{aligned} \langle n(x,0) \rangle = & \frac{1}{x \ln \epsilon_1 \sqrt{2\pi}} \zeta_1 \exp \left(-(\ln x - \ln \bar{x}_1)^2 / 2(\ln \epsilon_1)^2 \right) \\ & + \frac{1}{x \ln \epsilon_2 \sqrt{2\pi}} \zeta_2 \exp \left(-(\ln x - \ln \bar{x}_2)^2 / 2(\ln \epsilon_2)^2 \right) \end{aligned} \quad (19)$$

The values chosen for the ζ_1 , ϵ_1 , and $\bar{x}_1$ are discussed below.

RESULTS

From the results of the computer calculations we are able to comment on the role of sources on aerosol growth, the relative importance of photochemical production of aerosol, and the cause of the "brown cloud" color. The main inadequacies of the program--the volume averaged deposition and uncertainty of input data for the sources--are studied. We also include suggestions for improvements in the computer model and recommendations for further field study measurements.

The computer studies, outlined in Table 3, are divided into four categories. Runs 1 through 4 study the effects of modifying the deposition term. Run 5 examines the importance of photochemistry in aerosol production. Run 6 and run 7 show the influence of varying the source input distributions. For all of these runs advection and vertical mixing are constant. This means the mixing height is constant and the air parcel does not flow down the valley. In each run only one aspect of the model is varied. Since these are just case studies, the runs take place between nine o'clock and noon. Run 8 however, is a simulation over forty-eight hours and it includes all of the time dependent mechanisms.

The results of the computer runs are illustrated in Figure 9 through Figure 16. For each run the size distribution at various times is plotted as a function of particle diameter. In addition, the moments, total number, total mass and light scattering coefficient are plotted as a function of time. These moments are defined in the following way:

Table 3. COMPUTER STUDIES*

Computer Run	<u>Processes</u>					Time (Hours)	
	<u>Advection</u>	<u>Convection</u>	<u>Sources</u>	<u>Deposition</u>	<u>Condensation</u>		
				<u>Dry deposition</u>	<u>Gravitation-al settling</u>		
1	NV	NV	V	V	NV	V	9-12
2	NV	NV	V	O	NV	V	9-12
3	NV	NV	V	O	O	V	9-12
4	NV	NV	V	NV	NV	V	9-12
5	NV	NV	V	V	NV	O	9-12
6	NV	NV	V ⁺	V	NV	V	9-12
7	NV	NV	V ⁼	V	NV	V	9-12
8	V	V	V	V	NV	V	0-48

*NV $\equiv$ time independent, V $\equiv$ time dependent, O $\equiv$ omit

⁺ Source input distribution changed for combustion and point sources.

⁼ Source input distribution changed for dust sources.

$$\begin{aligned} \text{Total Number Concentrations, } N &= \int_0^{\infty} \langle n(x) \rangle dx & (20) \\ \text{Total Mass Concentration, } M &= \int_0^{\infty} \langle n(x) \rangle dx \\ \text{Light Scattering Coefficient, } b_s &= \pi/R^2 \int_0^{\infty} Q(\lambda/R, m) \langle n(x) \rangle dx \end{aligned}$$

where $Q(\lambda/R, m)$ is the light scattering efficiency factor obtained from Mie theory¹⁶. For the wavelength of the incident light, λ , we chose a typical nephelometer setting of 500 nanometers. The refractive index, m , is assumed to be (1.55-0.022i), a value that is believed to be in the correct range for the Denver aerosol¹⁷. To study the color effects in the Denver "brown cloud", b_{scat} is calculated as a function of wavelength and refractive index for the simulation run. For all the runs, the above values are assumed.

The parameter values for the initial distributions are given in Table 4. For the simulation run, a low background distribution is assumed¹⁵. For the shorter runs, the initial distribution is the nine o'clock distribution from the simulation run. Modifications of the source distribution parameters for run 6 and run 7 are listed in Table 5. Unless otherwise stated the distribution parameters are the same as those listed in Table 2.

Variation in deposition is studied because the results are most sensitive to this process. In Figures 9 through 12 we present the results of varying the form of the deposition term. In the first run the complete deposition term is used as defined in equation (9). In run 2, only gravitational settling is present. In run 3, deposition is omitted completely. Last, in run 4, the time dependence of dry deposition caused by changing wind speed is neglected. As one might expect, the aerosol grows most rapidly in the absence of deposition. The true deposition rate probably lies somewhere between the two extremes of no deposition and the complete deposition process.

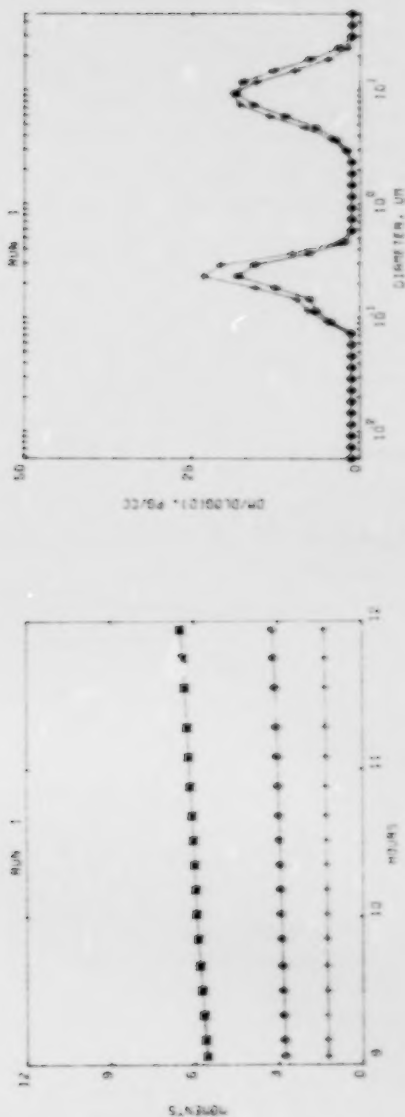
The importance of the photochemical production of aerosol is illustrated by run 5 for which condensation is neglected. A comparison of Figure 13 and Figure 9 shows that condensation has only a very small effect on the growth of the aerosol. Although growth of the "accumulation" mode (0.1 μm to 1.0 μm diameter range) is usually assumed to be evidence for photochemical activity, we find that this mode grows at almost the same rate in the absence of any photochemical input. This fact supports the idea that the aerosol is primarily source dominated. The conclusion--that photochemistry is not too important during the Denver pollution episodes--is reasonable considering the typical temperatures. It has been shown that photochemical reaction and subsequent aerosol growth are reduced by a significant amount¹⁸⁻²² at low temperatures such as are prevalent

Table 4. INITIAL DISTRIBUTION VALUES

<u>Run</u>	<u>Mean Value of DM/DLOG(D) Diameter (microns)</u>		<u>Variance</u>		<u>Magnitude of DM/DLOG(D)</u>	
	<u>Mode 1</u>	<u>Mode 2</u>	<u>Mode 1</u>	<u>Mode 2</u>	<u>Mode 1</u>	<u>Mode 2</u>
8	.2	3.0	5	5	.65	1.63
1-7	.2	9.0	5	5	18.0	18.0

Table 5. SOURCE TERM MODIFICATIONS

<u>Run</u>	<u>Source Changed</u>	<u>Particle Diameter</u>	
		<u>D_1 (μm)</u>	<u>β_1, Eq. 14</u>
6	Point sources and fuel combustion	0.6, 0.6	1.1, 1.1
7	Dust (construction and traffic)	20, 20	5, 5



MASS, cc X 10^{-11} - 0 -
 BSCAT, 1/cm X 10^{-7} - + -
 NUMBER, 1/cc X 10^4 - * -

HR 9 - 0 -
 HR 12 - + -

FIG. 9: RUN 1

The evolution of aerosol size distribution and moments for time dependent variables Sources, Dry Deposition, and Condensation and time independent variables Advection, Convection, and Gravitational Settling starting at HR 9 and ending at HR 12.

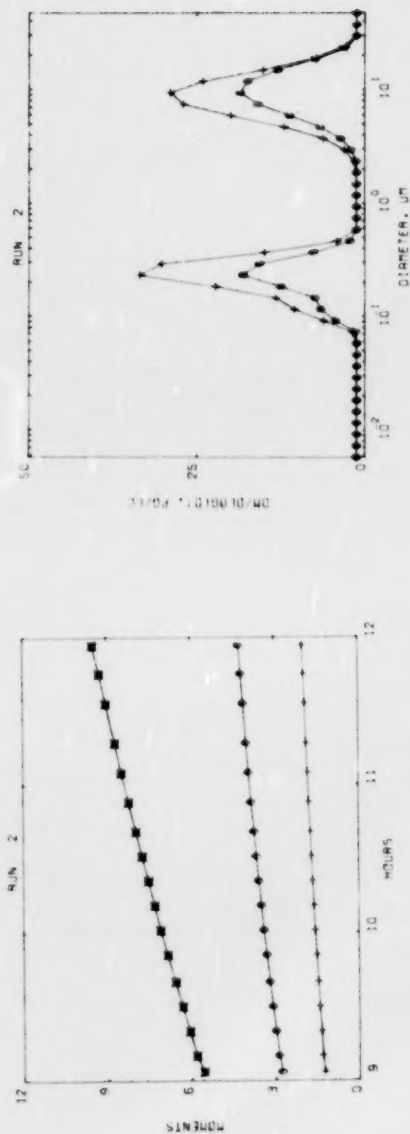
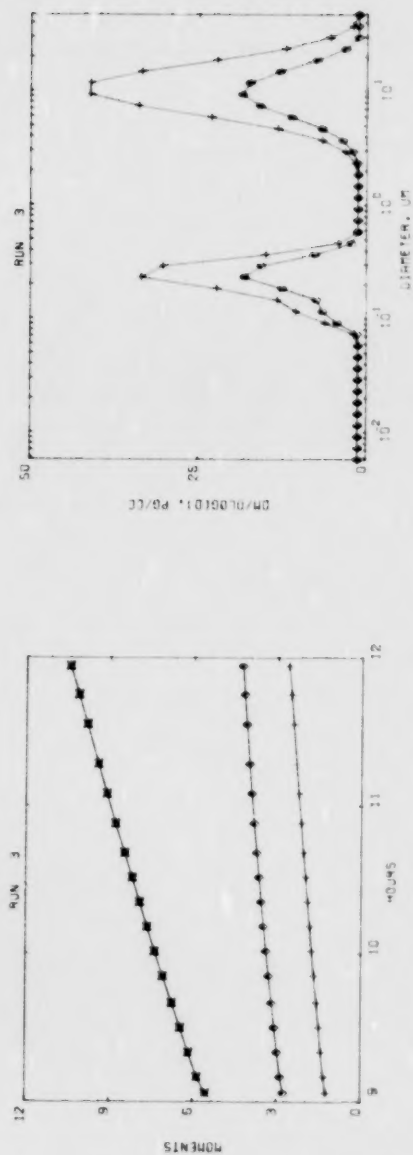


FIG. 10: RUN 2

The evolution of aerosol size distribution and moments for time dependent variables. Sources and condensation and time independent variables. Advection, convection, and gravitational settling starting at HR 9 and ending at HR 12. Dry deposition is omitted.

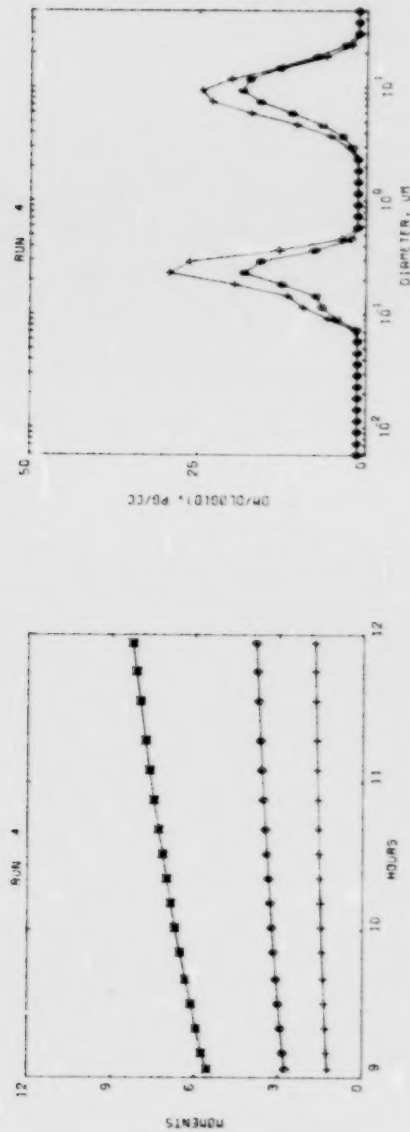


MASS, cc X 10^{-11} - 0 -
 BSCAT, 1/cm X 10^{-7} - + -
 NUMBER, 1/cc X 10^4 - * -

HR 9 - 0 -
 HR 12 - + -

FIG. 11: RUN 3

The evolution of aerosol size distributions and moments for time dependent variables. Sources and condensation and time independent variables. Advection and Convection starting at HR 9 and ending at HR 12. Dry deposition and gravitational settling are omitted.



MASS, cc X 10⁻¹¹ - 0 -
 BSCAT, 1/cm X 10⁻⁷ - + -
 NUMBER, 1/cc X 10⁴ - * -

HR 9 - 0 -
 HR 12 - + -

FIG. 12: RUN 4

The evolution of aerosol size distributions and moments for time dependent variables. Sources and condensation and time independent variables. Advection, convection, gravitational settling and dry deposition starting at HR 9 and ending at HR 12.

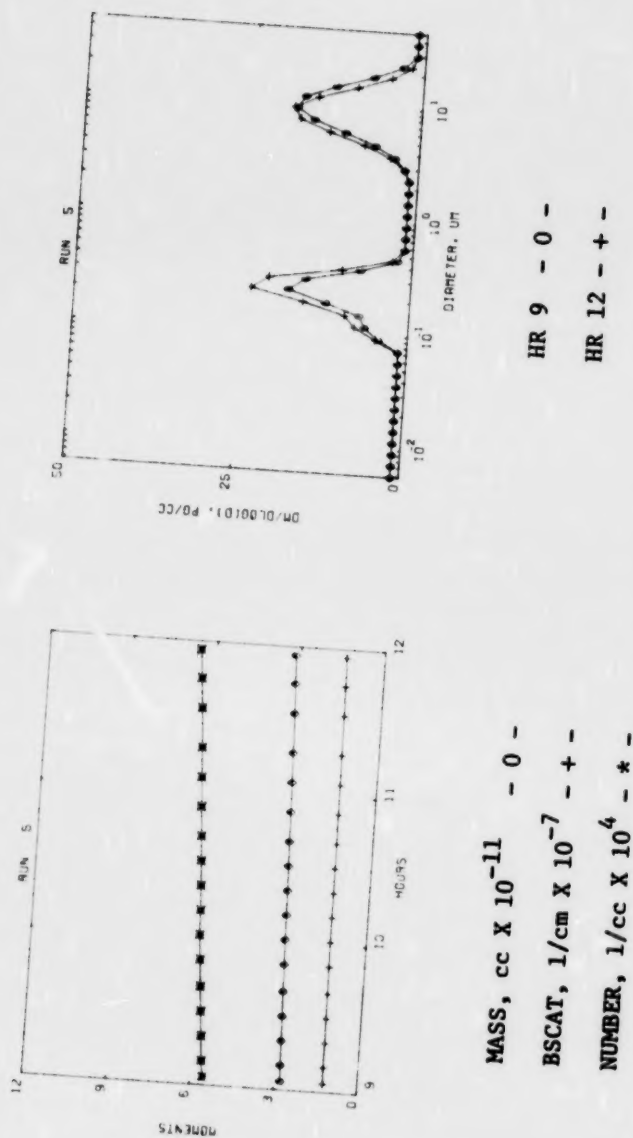


FIG. 13: RUN 5

The evolution of aerosol size distributions and moments for time dependent variables. Sources and dry deposition and time independent variables. Advection, convection and gravitational settling starting at HR 9 and ending at HR 12. Condensation is omitted.

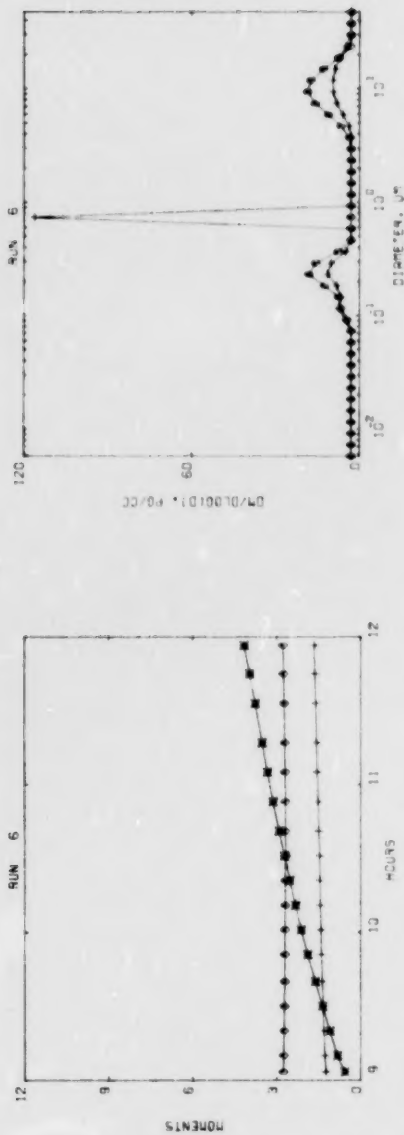
during a pollution episode in Denver.

The last aspects of the model to be considered are the sources. Since there are little data on the size distribution for the different source categories we took to be operating in Denver, we could only estimate distribution values^{5,11,12,13}. It would be particularly useful to have such measurements available for Denver since the selection of such parameters significantly affects the evolution of the aerosol. In run 6 we changed the point source and fuel combustion distribution by moving the peaks to a larger diameter. As seen in Figure 14 this shift gives rise to a rapidly growing, unrealistic third mode. In run 7 we shifted the dust distribution peak to 20 μm diameter. This mode, as shown in Figure 15, decreases at a faster rate than the coarse modes ($D > 1.0 \mu\text{m}$) in Figures 9-13. In fact, the coarse mode for run 7 can never grow, whereas the probability of accumulation is much higher when both the dust source distribution and the initial distribution are peaked at lower values of particle diameter. The sensitivity of the model to source input should be studied further. In addition, it would be desirable to obtain more detailed information about the source distributions for the Denver area.

The simulation study, run 8, is perhaps the most interesting run because we observe the slow build-up of aerosol over forty-eight hours, noticeable diurnal variation during the first day, and then follow the build-up of the aged aerosol during the second day. These results are illustrated in Figure 16. The total mass, total number, and bscat are all within the range of experimental observations^{8, 14, 15, 23}. We also see a definite correlation between bscat and the fine particle mode.

Since this model produces reasonable results when compared to field study measurements we can venture several conclusions about the Denver aerosol based on our calculations. The Denver episode aerosol is probably source dominated with photochemistry acting only as a minor secondary source. This means that the fine particle mode grows mainly by primary source input and coagulation. Since the coarse particle mode also oscillates in time, both coagulation and source input must be influencing its growth. The coarse mode never becomes too large because the larger particles are strongly affected by deposition. Condensation, which reflects the secondary source input, also affects both modes, but not to as great an extent as the other processes.

Several changes in the source term can produce variations in the magnitude of total mass, total number, and light scattering coefficient. These quantities are increased by raising the valley flow factor when the air parcel is outside of the city. This causes an increase in primary source input without changing the basic source term parameters derived from PEDCO study emission rates. Actually varying the emission rate for a particular source would

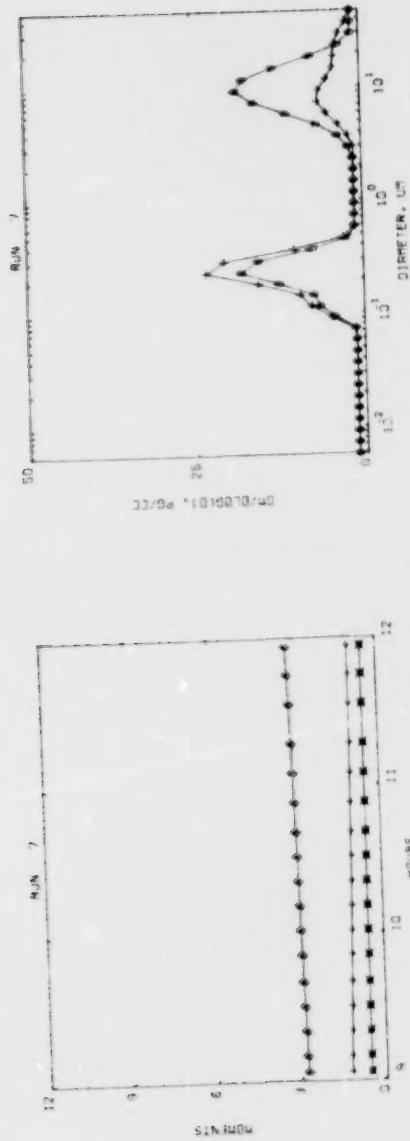


MASS, cc X 10^{-11} - 0 -
 BSCAT, 1/cm X 10^{-7} - + -
 NUMBER, 1/cc X 10^4 - * -

HR 9 - 0 -
 HR 12 - + -

FIG. 14: RUN 6

The evolution of aerosol size distributions and moments for time dependent variables. Sources, dry deposition and condensation and time independent variables. Advection, convection, and gravitational settling starting at HR 9 and ending at HR 12. Source input distribution is changed for combustion and point sources.



MASS, cc X 10⁻¹¹ - 0 -
 BSCAT, 1/cm X 10⁻⁷ - + -
 NUMBER, 1/cc X 10⁴ - * -

HR 9 - 0 -
 HR 12 - + -

FIG. 15: RUN 7

The evolution of aerosol size distributions and moments for time dependent variables. Sources, dry deposition, and condensation and time independent variables. Advection, convection, and gravitational settling starting at HR 9 and ending at HR 12. Source input distribution is changed for dust sources.

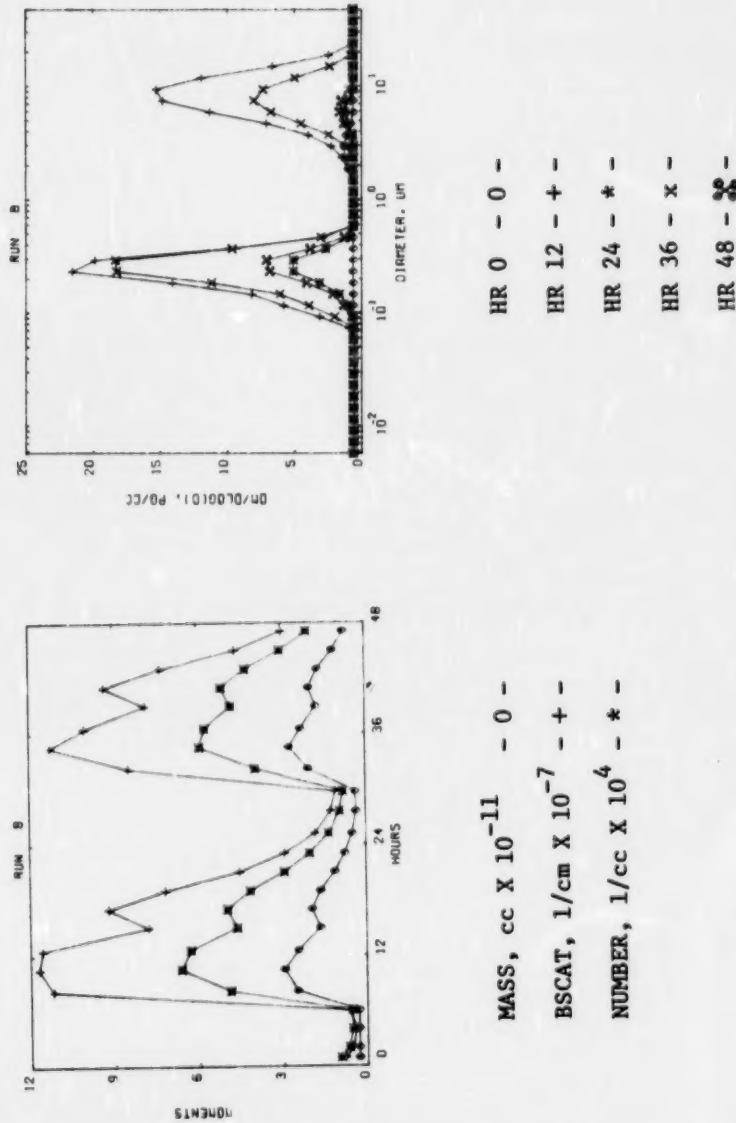


FIG. 16: RUN 8

The evolution of aerosol size distributions and moments for time dependent variables. Sources, dry deposition, condensation, advection, and convection and time independent variable gravitational settling starting at HR 0 and ending at HR 48.

would also modify the evolution of the particle size distribution. For example, if we assumed lower emission rates for the fine particle mode, we would expect the fine particle mode to be smaller and therefore, bscat also to be smaller. As we already illustrated in run 6 and run 7, changing the form of the source distribution mean and variance affects the evolution of the size distribution. Since the model is rather sensitive to the primary source input, further investigation of source distributions through field analysis would certainly help remove some of this ambiguity in the model.

We have studied the variation of bscat with wavelength and refractive index. These results are shown in Figure 17. It represents the calculation of bscat at wavelengths 430 nm, 530 nm, and 640 nm for the 9 a.m. size distribution from the 48 hour simulation run. The wavelengths chosen represent respectively the blue, green and red portions of the electro-magnetic spectrum¹⁷. Two refractive indices for the particles were chosen: (1.5, - 0.1i) and (1.5-0.01i).

The fact that bscat is higher for the smaller wavelengths suggests the light scattering by particles can contribute to the "brown cloud" effect. Although little is known in detail of the absorptive properties of the particle, an increase in the imaginary part of the refractive index (assuming that the imaginary part is not wave-length dependent), of course, lowers bscat and therefore would, within our assumptions, tend to diminish the importance of attenuation by scattering to the "brown cloud" effect.

It is possible that there may be several mechanisms contributing to the "brown cloud" effect. The wavelength dependence of attenuation by scattering could be one of these. However, this type of wavelength dependence is sometimes observed in other urban atmospheres²⁴. Therefore, the full explanation for the marked "brown cloud" effect in Denver must lie elsewhere. One can speculate that the large mode of the particle size distribution may exhibit wavelength dependent absorptive characteristics (the reddish soils of certain regions of Colorado, including the Denver area, have been noted by many visitors). Thus, multiple scattering (at episode (high) particle concentrations) and absorption may play some role in the "brown cloud". More detailed analyses than performed here may implicate differences in forward and back scattered light from the "brown cloud". In addition to the participation by particles, wavelength dependent light absorption by trace gaseous species could be of importance.

From the various simulation runs reported here (and many others which we have carried out) for Denver, we arrive at several conclusions. The ambient particle size distribution is very sensitive to the choice of parameters for the dry deposition rate and the primary source input rates; relatively small changes in these parameters results in values of mass concentration which disagree strongly with field data during episode conditions. This leads us to believe that our assess-

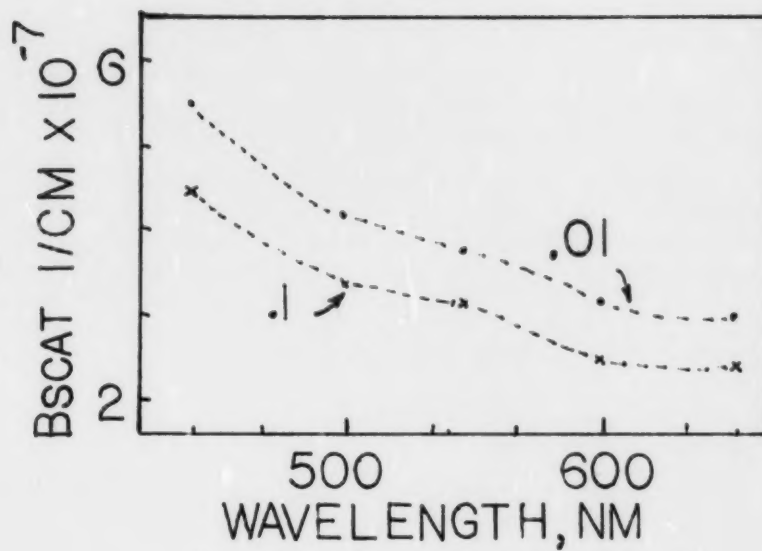


Fig. 17 Variation of Bscat with wavelength

Refractive index (1.5, - 0.01i) ----
Refractive index (1.5, - 0.1i) --X--

ment of these parameters does not contain appreciable error. We also conclude, as a result of our calculations plus various experimental observations^{8,14,15,23}, that the Denver episode aerosol is probably source dominated with photochemistry acting only as a minor secondary source. Thus the submicrometer particle mode grows mainly by primary source input and coagulation. The large particle mode is also influenced primarily by primary source input but also by deposition with some lesser but still appreciable effect of coagulation with combustion nuclei. Finally, the wavelength dependent light scattering by the episode aerosol has been shown to be a possible contributor to the "brown cloud" effect.

As noted earlier, a comprehensive model for the Denver aerosol is now under development. We believe that such a model can be a useful tool in the planning of field studies and interpretation of field study data. In addition, even with out present model (intended primarily to illustrate the basic features of the comprehensive model) it should be possible to test various control strategies for the Denver "brown cloud" and thereby to improve the air quality of this great city.

ACKNOWLEDGMENT

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NOMENCLATURE

Italic Letters

A	Millikan constant for particle mobility
A_1	Magnitude of source 1 distribution
B	Millikan constant for particle mobility
$b(x,x')$	Coagulation kernel
b_s	Light scattering coefficient
C	Millikan constant for particle mobility
D_1	Particle diameter corresponding to mass $\bar{x}_1$
$DW/DLOG(D)$	Particle mass distribution function
$F(t)$	Valley flow factor
g	Acceleration of gravity
$H(t)$	Mixing height
I_1	Emission flux for source 1
K	Kelvin coefficient
$L(t)$	Wind speed factor
M	Total mass concentration
m	Particle refractive index
N	Total number concentration
$n(x,r,t)$	Density function
$\langle n(x) \rangle$	Volume averaged density function
$Q(\lambda/R,m)$	Light scattering efficiency factor
R	Particle Radius
r	Space vector

S_j	Mass concentration of j^{th} chemical species
S_{jo}	Mass concentration of component j corresponding to vapor pressure of j over a plane liquid (or solid) surface
T	Temperature
t	Time
$U(x)$	Function fit to Sehmel's sedimentation velocity
u	Particle mean thermal speed
V_{jL}	Volume of a vapor molecule of j in the liquid (solid) phase
$V(x,t)$	Deposition velocity
$V_o(x)$	Gravitational settling velocity
$v(x,t)$	Time dependent component of the deposition velocity
$W(x)$	Source distribution function
x	Particle mass
$\bar{x}_i$	$\text{Ln}\bar{x}_i$ is mean for lognormal source distribution i

Greek Letters

$\alpha(x)$	Condensation coefficient
$\langle \alpha(x) \rangle$	Volume averaged condensation coefficient
β_i	Input for source i distribution variance ($\text{Ln}^2 \beta_i$)
γ	Surface tension at gas-particle interface
Δ	Particle diffusion constant

ϵ_1	Input for initial distribution mode 1 variance ($\ln^2 \epsilon$)
ζ_1	Magnitude of initial distribution mode 1
λ	Wavelength of incident light
μ	Gas viscosity
ρ	Particle density
$\langle \tau(x) \rangle$	Volume averaged deposition coefficient
τ	Time factor for source term
$\psi(x)$	Condensation coefficient
$\langle \psi(x) \rangle$	Volume averaged condensation coefficient
Ω	Gas mean free path

X-RAY FLUORESCENCE ANALYSIS OF DENVER AEROSOL

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ABSTRACT

Aerosol samples were collected in Denver during November, 1973, and were analyzed to determine which sources might contribute to the Brown Cloud phenomenon. A set of Low Volume samplers for collecting particles in the fine (less than 2 microns) and total size ranges was deployed at six sites, and an automatic device for making 2-hour average measurements was located at a site north of the city. The samples were analyzed for elemental composition with an x-ray fluorescence spectrometer. Most of the sulfur, bromine and lead was observed in the fine particles. By deduction, it was found that the crustal elements such as Al, Si, K, Ca, Ti and Fe occur mainly in the coarse particles (larger than 2 μm). The concentrations of several elements including lead, bromine, silicon, calcium, and iron and the gas, carbon monoxide, were found to be highly correlated with each other. Measurements of the light scattering coefficient were found to correlate best with a linear combination of the lead and sulfur concentrations. It is concluded that the automobile is a major source of the lead and bromine and causes crustal elements to be suspended, whereas the major sulfur sources are non-automotive.

INTRODUCTION

The scattering of light by atmospheric aerosols may be a major cause of the brown color of Denver's urban plume. As a means of determining the sources of these aerosols, a complete morphological classification as a function of size is needed. In the present work, an important part of the needed information is provided by x-ray fluorescence analysis of particulate matter collected on filters. X-ray fluorescence analysis is suitable for determining elements which have atomic numbers above 12; these include Al, Si, K, Ca, Ti and Fe, the major metal constituents of soil dust. It also includes S, whose major source is often the burning of fossil fuel, Br and Pb from auto exhaust and several trace elements from a variety of sources.

Since the scattering of light by particles is strongly size-dependent, it is important that the analysis be carried out on size fractionated samples. In the present experiment, aerosol samples were collected, during November of 1973, in two size ranges, using a Low Volume Sampler developed by Marple (1). For this device, the filters were changed manually as frequently as once every eight hours. An additional automated sampler which changed filters every two hours was also used. The two-hour sampling duration was short enough for investigation of the correlations between elemental concentrations measured on the filters and the light scattering coefficients measured with an integrating nephelometer.

PROCEDURE

Size fractionated aerosols were collected with the Low Volume sampler (1) which is illustrated in Figure 1. Fine particles, with diameter less than 2 microns, were collected on a filter preceded by a jet impactor. The impaction surface was coated with silicon grease. Particles of all sizes were collected on a second filter. Both samplers were oriented upwards without a rain shield in order to collect with high efficiency the fine and coarse particles. The elemental concentrations of the coarse (diameter greater than 2 microns) particles were deduced by taking the difference between the measurements on the pair of filters. The coarse particles collected on the impactor were not analyzed.

For the Low Volume Samplers, the flow rates were controlled with critical flow orifices rated at 14 liters per minute. Millipore Type AA filters of 37 mm diameter were used in plastic filter holders shown in Figure 1. After the sampling was complete, the holders were covered and sent back to the laboratory for analysis.

In order to make a sequence of measurements over two-hour intervals, an automated sampler was also used. The device operated at a flow rate of 50 liters per minute through the inner 32 mm diameter of Millipore Type AA filters. The filters were premounted in 5.1 x 5.1 cm square plastic frames to facilitate automatic manipulation. Although no specific

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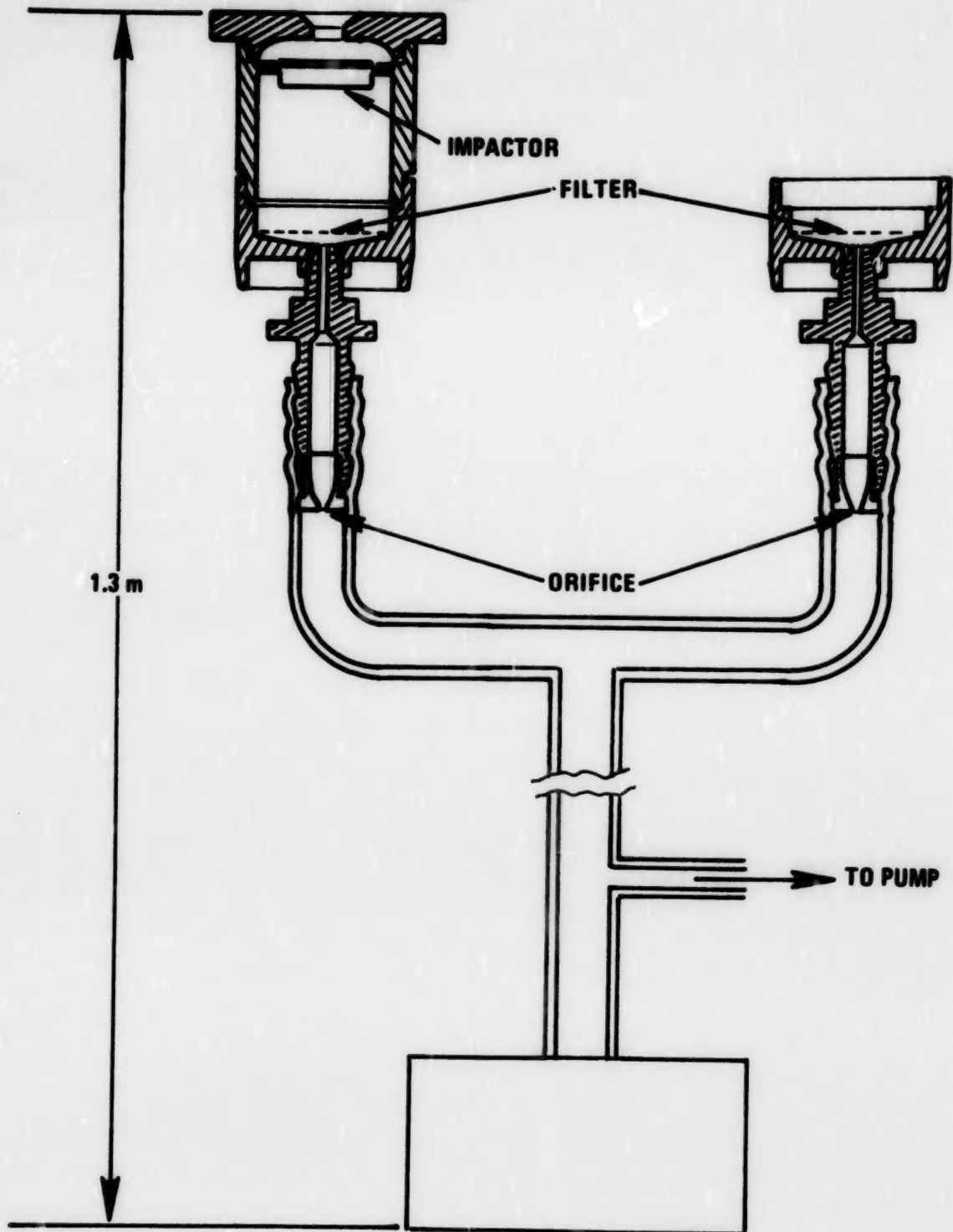


FIGURE 1. Cross-sectional view of Low Volume Sampler

size fractionators were used, the inlet plumbing caused particles larger than about 15 μm in diameter to be lost on the walls.

To obtain a representative measurement of Denver aerosol, the Low Volume Samplers were deployed at six sites located in a north-south line along the South Platte River. The locations of the sites are shown in the map on Figure 2 and are specifically identified as Henderson Fair Grounds (HF), Trout Farm (TF), Welby (WB), General Motors Assembly Plant GM, EPA CAMP Station (CP) and Denver Research Institute (DR). The automated sampler was placed inside the AARS mobile laboratory located at the Trout Farm site, where several other parameters, including wind speed, carbon monoxide and light scattering coefficients were measured. A summary of the measurements which were made from November 6 to 21, 1975, is given in the Appendix in Tables A1 and A4.

After the field sampling was complete, the collected aerosols were analyzed for elements with atomic numbers above 12 with an energy-dispersive x-ray fluorescence spectrometer. In the spectrometer, an x-ray tube with a tungsten anode was used to excite a secondary fluorescer, which in turn excited the sample with its nearly monochromatic characteristic x-rays (2). Each sample was excited for 5 minutes using both titanium and molybdenum secondary fluorescers in order to excite elements with atomic numbers in the intervals 13-20 and 19-38, respectively. Lead was also measured using the molybdenum fluorescer. Several of the samples were also analyzed using a samarium fluorescer in order to excite elements with atomic numbers between 38 and 57. Measurements of the spectrum of x-rays from the sample were made with a lithium-drifted silicon detector. The spectra were analyzed using a stripping procedure to determine the contribution from each element. A correction for the lead α x-ray interference with sulfur was made based on the strength of the measured lead L_{β} intensity. A small computer was used to control the spectrometer and to perform the analysis.

The analyzer was calibrated with vacuum-deposited foils for each element using a procedure developed by Giauque et. al. (3). The deposits were prepared by Micromatter, Inc., Seattle, Washington, and they ranged from 50 to 150 $\mu\text{g}/\text{cm}^2$ in mass per unit area. For airborne particles uniformly deposited onto a filter, the concentration (in ng/cm^2) of a specific element was determined by comparing the observed count rate with that of the known foil of the same element. For light elements, an additional correction was made for self absorption effects using a procedure developed by Dzubay and Nelson (4).

In the above manner, the spectrometer was calibrated to measure aerosol deposits in units of ng/cm^2 . The measurements were later converted to units of ng/m^3 by dividing by the air volume sampled per unit area of filter. For 8 hours of operation of the Low Volume Sampler at a flow rate of 14 liters per minute through a deposit area of 9 cm^2 , the conversion factor is 0.74 m^3/cm^2 . For two hours of operation of the automatic sampler at a flow rate of 50 liters per minute through an area of 8 cm^2 , the conversion factor is 0.75 m^3/cm^2 . These conversion factors are based upon the assumption that the deposits are uniform across the filter.

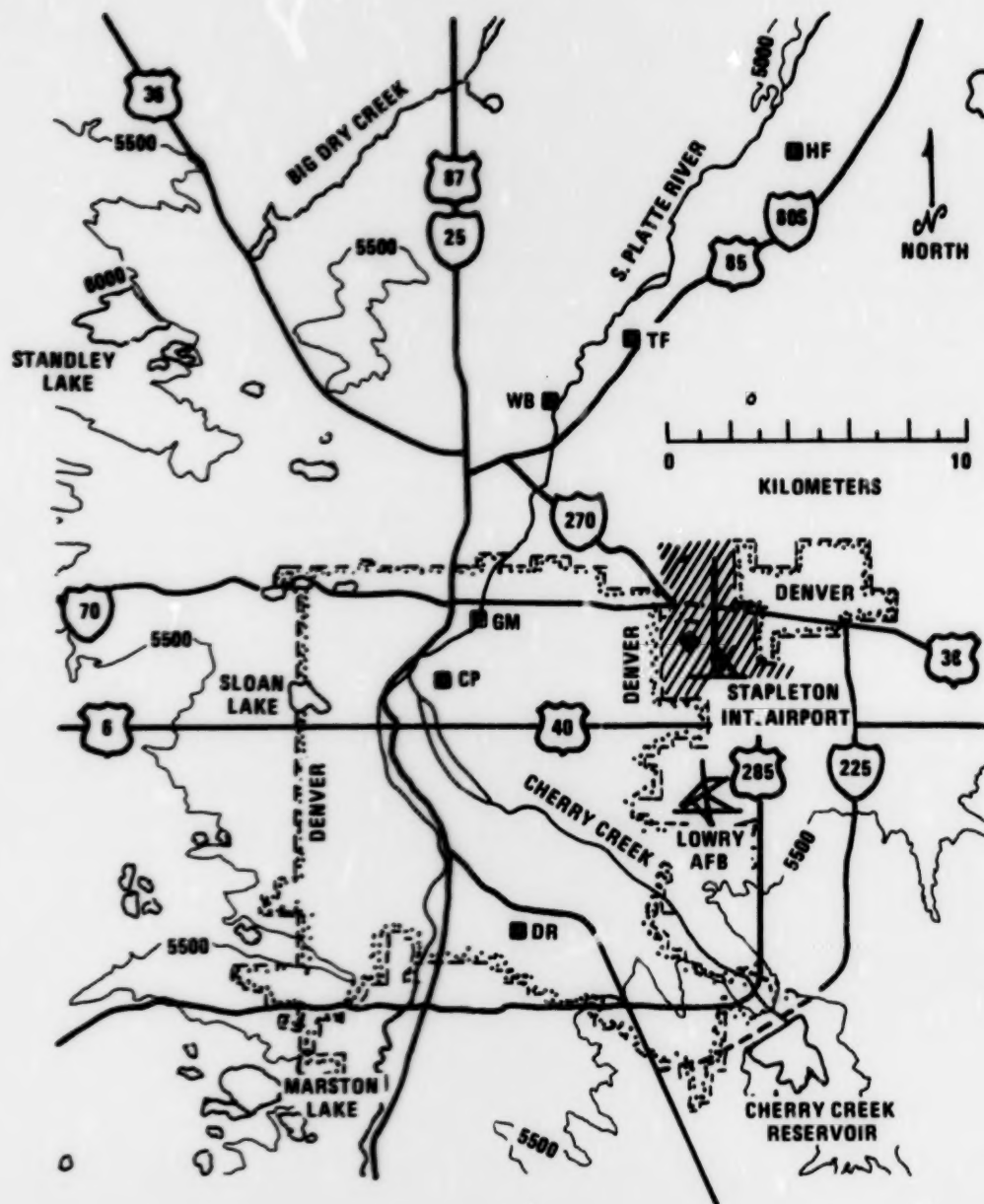


FIGURE 2. Map of Denver area. The sampling sites are shown as solid squares (■). Major highways and elevation contours (in feet above mean sea level) are also shown.

RESULTS

A tabulation of all of the required measured results is given in the Appendix in Tables A1 and A4. The tabulated elemental concentrations were deduced from the procedure described above. Whenever the concentration of an element was smaller than the detection limit (2), the results were reported as being less than the detection limit as shown in Table A1. Table A1 shows only those elements which frequently occurred at concentrations well above the detection limits. The concentrations of P, Cl, Cr, Co, Ni, Ga, Ge, As, Se, Rb, Pt, Au and Hg were usually at or below the detection limit. The accuracy for each element is estimated to be either the detection limit or 15 percent of the concentration, whichever is larger. Each sample was examined for uniformity of deposit and for integrity of the filter. In a few instances, the deposits were nonuniform or the filters were cracked, and such cases are noted in Table A1.

The elemental concentrations for the 2-hour averaged measurements at the Trout Farm are given in Table A4. Also given are 2-hour averaged values of the light scattering coefficient (BSCAT), carbon monoxide (CO) and wind speed (WSPD) measured by Durham et al (5).

DISCUSSION

There is a striking difference between the composition of the fine and coarse particles. According to Table A1, at least 75 percent of the S, Br and Pb occur in fine particles (smaller than 2 μm). On the other hand, Al, Si, K, Ca, Ti, Mn and Fe occur predominantly in the coarse particles (larger than 2 μm). This is identical to an effect observed previously in St. Louis by Dzubay and Stevens (6).

It is suggested that the various elements originate from different sources. Lead and bromine would most likely come from automobiles as components of exhaust. The elements such as Al, Si, K, Ca, Ti, Mn and Fe are expected to come from wind-blown minerals and fly ash. The sulfur in the fine particles probably originated as SO_2 from power generators, motor vehicles and petroleum refining and was later converted to sulfate in the atmosphere.

Interelement Ratios

The ratios of measured concentrations for pairs of elements are given in Table 1. The ratios of Al, Si, K, Ca and Ti to Fe are similar to the values for the average earth's crust (7) and to the values for the soil samples from Denver (8), which are also given in Table 1. The similarity of these ratios suggests that possibly this group of elements in the Denver aerosol are associated with wind-blown mineral dust. However, microscopic examination showed that the fly ash content varied

from several percent to greater than 25 percent, indicating that the fly ash also has elemental ratios similar to the average earth's crust (5). In relation to the crustal elements, the relative concentrations of lead, bromine and sulfur in the aerosol are elevated by large factors. Automotive emissions are likely the major source of lead and bromine in the fine aerosol fraction. The measured lead to bromine ratios of 0.26 to 0.30 are typical of values seen in another study (6) and are comparable to the value of 0.39 for PbClBr. Automotive emissions are also the major source of the carbon monoxide. The presently measured carbon monoxide to lead ratio of 1.2 ppm per $\mu\text{g}/\text{m}^3$ is comparable to the value 1.1 ppm per $\mu\text{g}/\text{m}^3$ which is an average measured at freeway sites in various parts of the country (9). On the other hand, the automotive emissions cannot be the major source of the sulfur in the aerosol. The average measured sulfur concentration of the atmospheric aerosol exceeds that of lead by a factor of about 3, whereas the sulfur to lead ratio in gasoline is typically only 0.5 (10). Moreover, automotive sources would not have emitted the sulfur as an aerosol, but rather as sulfur dioxide gas (for the non-catalyst-equipped cars of this 1973 study).

Table 1. RATIOS OF ELEMENTAL CONCENTRATIONS (a)

Elements	All Lo Vol Sites	Trout Farm 2-hr Data	Earth's Crust(b)	Denver Soil(c)
Al:Fe	2.8	4.8	1.6	2.9
Si:Fe	5.2	5.4	5.5	21(c)
S:Fe	2.9	6	0.01	
K:Fe	0.7	0.6	0.52	
Ca:Fe	0.8	0.8	0.73	0.9
Ti:Fe	0.11	0.16	0.088	
Pb:Fe	1.3	2.1	0.0003	0.014
S:Pb	2.3	4.1		
Br:Pb	0.26	0.30		
CO:Pb		1.2 ppm per $\mu\text{g}/\text{m}^3$		

(a) Averages of the ratios for each measurement. Measurements below detection limits are not included.

(b) Ref. (7).

(c) Ref. (8) - The results for Si may be high due to the use of a silicon hammer for crushing the sample.

Interelement Correlations

In order to examine the above suggestion that the various elements originate from specific sources, correlation coefficients were calculated for each pair of elements. For the Low Volume Sampler data of Table A1, only the unfractionated size range was used, and the results are given in Table A2. For the two-hour averages of Table A4, the correlation coefficients are given in Table A5. Coefficients of linear regression are given in Table 2. Plots of pairs of elemental concentrations and linear regression lines are given in Figure 3.

According to Table 2, there are very high correlations among elements in the crustal group which includes Al, Si, K, Ca, Ti and Fe. There are also very high correlations among Pb, Br and carbon monoxide of auto exhaust. It is important to note that there are also high correlations between crustal elements and components of auto exhaust. For example, the correlation coefficients are 0.91, 0.94, 0.94 for the pairs Pb-Fe, respectively, from the two-hour averages. These high correlations are not explained by asserting that lead and bromine occur in the same particles as do the crustal elements. This is clearly not the case, because the crustal elements occur predominantly within the coarse particles, whereas Pb and Br occur primarily within the fine particles. A more likely explanation is that combustion aerosol is generated by the burning of gasoline at the same time that the automobiles are mechanically generating a road dust aerosol.

Sulfur is very poorly correlated with all of the other measured species. Copper is also poorly correlated with other measured species in the aerosol. The only exception is a high correlation between copper and calcium at the CAMP Station site. The copper concentrations were relatively high at this site, indicating a possible source nearby.

There is a weak negative correlation between wind speed and both the crustal elements and the components of auto exhaust. The plot of iron concentration vs wind speed in Figure 3 indicates that the highest wind speeds are associated with the lowest iron concentrations and vice versa. Hence, the wind may be serving as a means of ventilation for pollutant removal. This is contrary to the familiar experience of high winds introducing soil dust into the atmosphere. However, the maximum wind speed in the present experiment for which correlations were computed was only 20 km/hour. According to studies by Newman et al, the wind becomes an effective dust generator only when the speed exceeds about 20 km/hour (11).

Table 2. CORRELATION COEFFICIENTS BETWEEN VARIOUS ELEMENTS IN UN-FRACTIONATED AEROSOL SAMPLES. For the Low Volume Samplers, the number of measurements is shown in parentheses.

	LOW VOLUME SAMPLERS		2 HOUR AVERAGES	
	All Sites (50)	Camp Station (5)	Trout Farm (11)	Trout Farm
<u>MINERAL GROUP</u>				
Si-Al	0.94	0.98	0.91	0.94
Si-K	0.98	0.99	0.99	0.98
Si-Ca	0.89	0.89	0.98	0.83
Si-Ti	0.92	0.99	0.93	0.91
Si-Fe	0.98	0.98	0.98	0.96
<u>AUTO EXHAUST</u>				
Pb-Si	0.84	0.73	0.77	0.89
Pb-Fe	0.83	0.77	0.82	0.91
Pb-Br	0.97	0.94	0.94	0.97
CO-Si				0.94
CO-Fe				0.94
CO-Br				0.95
CO-Pb				0.97
<u>SULFUR</u>				
S-Si	0.05	0.20	-0.40	-0.10
S-Ca	0.36	0.54	-0.42	-0.26
S-Fe	0.10	0.28	-0.46	-0.15
S-Pb	-0.02	-0.49	-0.34	-0.11
<u>LIGHT SCATTERING</u>				
BSCAT-Si				0.21
BSCAT-S				0.48
BSCAT-S				0.24
BSCAT-Pb				0.40
BSCAT- $[\frac{1}{2}(S) + (Pb)]$				0.67
<u>WIND SPEED</u>				
WSPD-Si				-0.49
WSPD-S				-0.07
WSPD-Fe				-0.54
WSPD-Pb				-0.49
<u>OTHER</u>				
Cu-Si	0.55	0.78	0.21	
Cu-Ca	0.83	0.98	0.29	
Cu-Fe	0.59	0.72	0.30	
Cu-Pb	0.46	0.30	0.15	

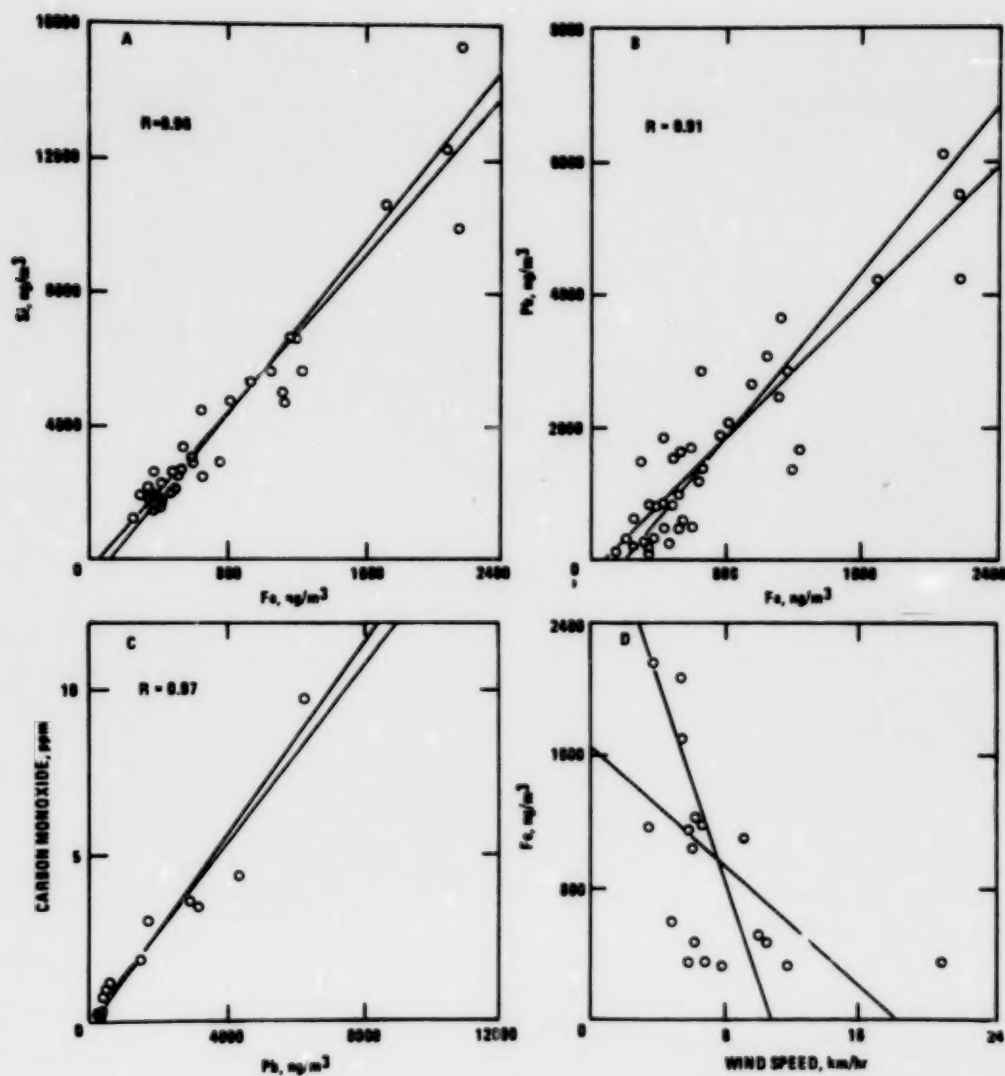


FIGURE 3. Linear regression plots for various pairs of measured parameters. The data represent two-hour averages measured at the Trout Farm site during November, 1973.

Light Scattering

Since the scattering of light by aerosols is a major cause of visibility degradation, valuable clues about the Brown Cloud problem can be gotten by examining the light scattering measurements made with an integrating nephelometer. Of all the atmospheric particles, the fine particles in the 0.1 to 2 μm range are expected to have the greatest effect on light scattering (12). Hence, the sulfur, lead and bromine (as well as unmeasured soot and carbon compounds in the fine particles) are expected to correlate best with the light scattering coefficient. According to Table 2, the correlation coefficients are a meager 0.40 and 0.48 for lead and sulfur respectively. When the quantity $[\frac{1}{2}(\text{S}) + (\text{Pb})]$ is compared with the light scattering coefficient, a much better correlation of 0.67 is obtained. A plot of the above quantity is given in Figure 4.

From these data it appears that the light scattering is caused both by auto exhaust, for which lead is a tracer, and by some other source, for which sulfur is a component. This observation is based on a rather small number of measurements. Additional measurements would be needed before a great deal of confidence could be placed on this observation.

CONCLUSIONS

The following conclusions can be drawn from the present analysis of the Denver aerosol samples collected during November, 1973:

- Most of the S, Br and Pb occur in fine particles. The elements in the crustal group consisting of Al, Si, K, Ca, Ti and Fe occur predominantly in the coarse particles.
- For the coarse particles in the crustal group of elements, the ratios of concentrations between elements are similar to the values for the average earth's crust.
- The correlations among members of the crustal group are very high.
- The correlations are very high among the auto exhaust components such as Br, Pb and carbon monoxide.
- There is a poor correlation between sulfur and all other measured species.
- The light scattering coefficient correlates fairly well with the quantity $[\frac{1}{2}(\text{S}) + (\text{Pb})]$, indicating that the sources of both the sulfur and the lead contribute to visibility degradation.
- Additional measurements at more than one site using an integrating nephelometer, a carbon monoxide analyzer and an automatic sampler are needed before the above conclusions have adequate statistical validity for establishing policy for control of pollutants.

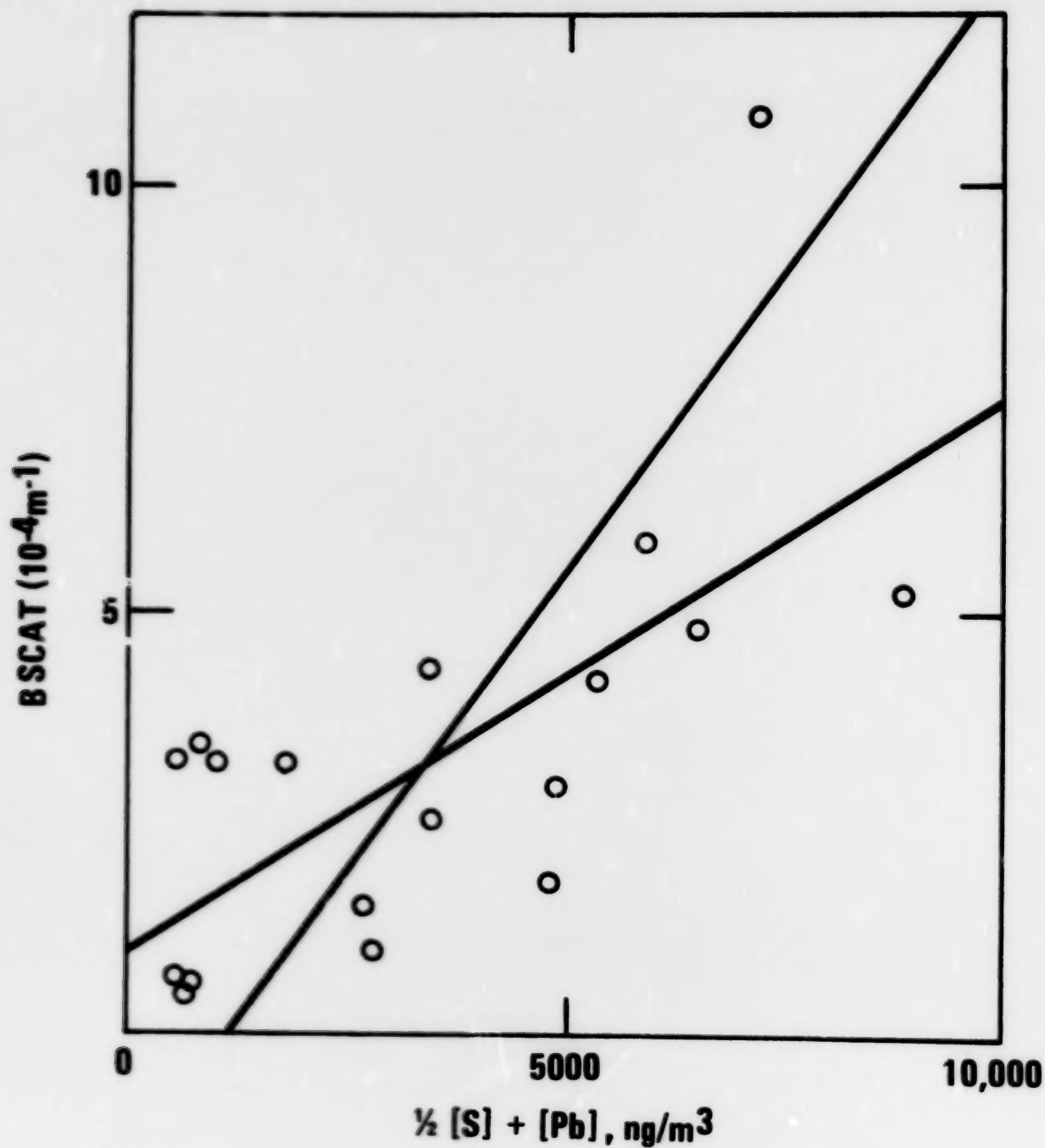


FIGURE 4. Light scattering coefficient vs. sum of lead and $\frac{1}{2}$ of sulfur concentrations for two-hour averages at the Trout Farm site.

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APPENDIX

Correlation coefficients were calculated for all pairs of measured concentrations according to the expression

$$r_{xy} = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{[\sum (x - \bar{x})^2 \sum (y - \bar{y})^2]}}$$

Coefficients of linear regression for a best fit to the data with the linear equation

$$y = A + Bx$$

were calculated according to the expressions

$$A = \frac{\bar{y} \sum x^2 - \bar{x} \sum xy}{\sum (x^2 - \bar{x}^2)}$$

$$B = \frac{\sum (xy - \bar{x}\bar{y})}{\sum (x^2 - \bar{x}^2)}$$

In the above summations the subscripts i have been omitted;

x_i and y_i are individual measured concentrations, and

$\bar{x}$ and $\bar{y}$ are average values for the data sets (x_i) and (y_i) respectively.

FOOTNOTES TO TABLES A1 - A6

Units

Elemental Concentration:	ng/m ³
Wind speed (WSPD):	km/hr
Light Scattering Coefficient (BSCAT):	10 ⁻⁴ m ⁻¹
Carbon monoxide (CO):	parts per million

Size Parameter

Size 0:	all sizes; no fractionation
Size 1:	fine particles; less than 2 μm

Note Parameter

Note 0:	highly nonuniform deposits, qualitative results only
Note 1:	cracked filter
Note 2:	good quality deposits
Note 3:	fine and total size range labels seem to be interchanged or incorrect

Using the data sets in tables A1 and A4, correlation coefficients are given in Tables A2 and A5, and coefficients of linear regression are given in Tables A3 and A6 respectively. Of the Low Volume Sampler measurements, only the data with size range code 0 and note code 2 were used in the calculation of correlation coefficients.

TABLE A1. LOW VOLUME SAMPLER DATA

SITE	SIZE	DATE	TIME	INT.	ID	NOTE	VOLUME	CONCENTRATION (NANOGRAMS PER CUBIC METER)														SR	PB
								AL	SI	S	K	CA	TI	V	MN	FE	CU	ZN	BR				
DR	0	06	0800-1600	73033	2		6.72	1874	4233	752	448	430	495	432	28	714	47	117	212	13	1019		
DR	1	08	0800-1600	73035	2		6.72	<1663	<983	<650	446	430	495	<32	<22	63	41	32	166	<12	803		
DR	0	08	1600-2400	73034	2		6.72	<1663	1098	4650	585	430	495	432	237	60	38	89	<12	201			
DR	1	08	1600-2400	73036	2		6.72	<1663	<983	<650	406	430	495	<32	<22	<31	32	<12	51	<12	178		
DR	0	09	0000-0800	73019	2		6.72	1799	2401	5066	4906	430	495	432	34	491	36	154	434	<12	1489		
DR	1	09	0000-0800	73020	2		6.72	<1663	<983	3718	4906	430	467	<32	59	84	74	151	420	<12	1120		
DR	0	09	0800-1600	73037	2		6.72	4861	10498	4026	1564	1634	169	45	40	1862	47	151	679	18	3360		
DR	1	09	0800-1600	73038	2		6.72	<1663	<983	3718	4906	430	467	<32	23	63	51	74	458	<12	2409		
DR	0	09	1600-2400	73045	2		6.72	10520	21935	3625	3060	3234	438	41	85	4273	51	339	1450	47	5050		
DR	1	09	1600-2400	73046	2		6.72	1934	<983	3425	4906	430	467	<32	27	176	38	175	1090	<12	3669		
DR	0	10	0000-0800	73043	2		6.72	<1663	2387	<650	4906	430	467	<32	<21	486	38	74	74	<12	326		
DR	1	10	0000-0800	73044	2		6.72	<1663	<983	<650	4906	430	467	<32	<21	<31	<24	61	51	<12	250		
DR	0	10	0800-1600	73040	2		6.72	<1663	2661	<650	4906	430	467	<32	<21	476	<24	27	192	<12	788		
DR	1	10	0800-1600	73042	2		6.72	<1663	<983	<650	4906	430	467	<32	<21	39	<24	<12	145	<12	557		
DR	0	10	1600-2400	73041	2		6.72	4920	8917	<650	1221	627	146	<32	41	1630	51	179	571	18	2139		
DR	1	10	1600-2400	73039	2		6.72	<1663	<983	<650	4906	430	467	<32	<21	103	38	122	449	<12	1620		
DR	0	14	0804-1700	73075	2		7.50	2795	5822	4582	766	1055	117	35	34	1156	37	37	168	16	823		
DR	1	14	0804-1700	73128	2		7.50	<1490	<880	4582	4364	4385	478	<29	<19	52	24	11	109	<10	563		
DR	0	16	0000-0800	73070	2		6.72	<1663	2767	<650	4906	430	467	<32	<21	696	36	127	192	<12	571		
DR	1	16	0000-0800	73110	2		6.72	<1663	<983	<650	4906	430	467	<32	<21	103	47	137	112	<12	456		
DR	0	21	0000-0800	73173	2		6.72	<1663	3193	<650	457	430	467	<32	23	502	36	151	83	<12	344		
DR	1	21	0000-0800	73200	2		6.72	<1663	<983	<650	4906	430	467	<32	<21	<31	36	112	65	<12	203		
DR	0	21	0800-1600	73181	2		6.72	2172	6080	<650	802	567	467	41	23	923	41	56	235	<12	1190		
DR	1	21	0800-1600	73174	2		6.72	<1663	<983	<650	4906	430	467	<32	<21	<31	36	23	160	<12	813		
CP	0	06	0000-0800	73077	0		6.72	<1663	1461	<650	4906	430	467	<32	<21	256	<24	27	122	<12	495		
CP	1	06	0000-0800	73079	2		6.72	<1663	<983	<650	4906	430	467	<32	<21	49	32	13	89	<12	401		
CP	0	06	1600-3230	73201	2		13.86	4906	11433	1091	1476	2094	300	37	142	2862	100	559	1340	31	4939		
CP	1	06	1600-3230	73202	2		13.86	1459	638	1157	<196	<208	<42	<15	59	243	73	407	920	<5	3300		
CP	0	07	0830-1530	73021	2		5.88	<1899	<1124	<742	4464	4491	<100	<37	<25	197	150	155	567	<13	4349		
CP	0	07	1530-2400	73026	0		7.14	3477	6208	988	765	869	106	<30	44	1335	70	151	1060	13	3509		
CP	1	07	1530-2400	73025	2		7.14	<1565	<925	800	<382	<404	<82	<30	<20	84	44	66	767	<11	2430		
CP	0	08	0000-0800	73081	0		6.72	4181	5629	4918	530	855	120	<32	51	1272	41	65	473	27	1599		
CP	1	08	0000-0800	73082	2		6.72	<1663	<983	3706	4906	430	467	<32	<21	<31	41	13	302	<12	921		
CP	0	09	0800-1500	73047	2		5.88	12793	25322	9838	3204	6604	684	70	166	5957	576	421	907	118	4499		
CP	1	09	0800-1500	73048	2		5.88	2590	1498	8160	<464	<491	<100	<37	70	447	486	194	611	<13	3219		
CP	0	10	1600-2400	73049	2		6.72	8772	20604	962	2998	2792	476	45	94	4194	109	410	1544	47	5829		

TABLE A1. (CONT.) LO VOL DATA

SITE	SIZE	DATE	TIME	INT.	ID	NOTE	VOLUME	CONCENTRATION (NANOGRAMS PER CUBIC METER)													
								AL	SI	S	K	CA	TI	V	MM	FE	CU	IN	SR	PS	
CP	1	10	1400-2400	73050	2		6.72	1784	4983	4650	4906	4930	487	432	421	267	65	179	1189	412	1060
CP	1	14	0000-0430	73100	2		7.96	1184	4827	4548	4342	4362	473	427	418	426	30	410	196	410	579
MF	1	04	0000-0800	73010	2		6.72	1407	4983	1461	4906	4930	487	432	421	37	38	13	36	412	260
MF	0	04	0800-1400	73008	2		6.72	1765	2709	1574	4946	4930	487	41	421	585	61	27	120	412	426
MF	1	04	0800-1400	73011	2		6.72	1407	4983	1524	4946	4397	487	432	421	37	41	412	104	412	509
MF	0	04	1400-2400	73009	2		6.72	1676	2772	1397	4946	410	148	432	23	596	38	41	160	13	466
MF	1	04	1400-2400	73012	2		6.72	1407	4983	1188	4946	4397	495	430	421	43	32	27	104	412	482
MF	0	04	0810-1400	73028	2		6.58	2709	2272	8832	4954	4905	497	431	423	354	33	24	91	18	453
MF	1	04	0810-1400	73027	2		6.58	1542	41004	6921	4954	4905	497	431	423	431	42	412	66	412	342
MF	0	14	0000-0800	73137	2,3		6.72	1618	3837	4625	636	613	495	430	34	726	41	34	278	412	692
MF	1	14	0000-0800	73104	2,3		6.72	2921	6579	3192	776	843	105	47	85	1290	56	168	604	18	1840
MF	0	14	0807-1135	73123	2		2.91	3498	7838	41444	1065	971	4221	471	103	1390	75	75	426	428	1829
MF	1	14	0807-1135	73104	2		2.91	4349	2450	41444	1030	918	4221	471	57	436	109	42	478	428	1719
MF	0	14	0000-0800	73129	2		6.72	3538	6446	4625	892	1140	197	36	50	1359	41	137	244	18	877
MF	1	14	0000-0800	73116	2		6.72	1586	2853	6325	4946	4397	495	430	50	594	47	104	198	13	726
MF	0	14	0805-1400	73109	2		6.65	1642	3998	4632	514	605	466	430	423	726	42	13	57	14	304
MF	1	14	0805-1400	73132	2		6.66	4121	1772	4632	4949	4901	496	430	423	291	42	18	61	412	309
MF	0	14	1406-2400	73107	2		6.64	4094	16129	4632	2328	1706	283	430	75	2639	47	71	482	18	1690
MF	1	14	1406-2400	73122	2		6.64	2249	5677	4632	785	504	123	430	28	936	33	33	392	412	1319
MF	0	17	0010-0800	73119	2		6.58	5536	13016	680	1724	1558	221	48	60	2379	52	182	1170	18	3639
MF	1	17	0010-0800	73146	2		6.58	2709	4254	4638	676	476	497	431	35	844	42	132	1049	412	2049
MF	0	17	0404-1400	73117	2		6.64	2673	7129	793	862	874	149	430	75	1359	37	81	190	14	884
MF	1	17	0404-1400	73170	2		6.64	4123	1596	723	4951	4902	496	430	44	328	42	62	156	412	744
MF	0	17	1408-2400	73115	2		6.61	2153	6491	4635	829	560	111	431	423	1079	33	27	183	412	434
MF	1	17	1408-2400	73180	2		6.61	4130	2112	4635	4953	4904	496	431	423	326	33	13	129	412	451
MF	0	21	0000-0800	73153	2		6.72	3492	7429	2358	1080	1352	184	42	59	1510	51	112	425	27	1420
MF	1	21	0000-0800	73152	2		6.72	4107	1479	1782	4946	4397	495	430	24	331	36	86	344	412	1069
MF	0	21	0810-1400	73154	2,3		6.58	4136	1182	2358	4954	4905	497	431	423	146	38	412	149	412	626
MF	1	21	0810-1400	73151	2,3		6.58	2192	3822	2691	599	610	112	33	35	675	48	28	157	18	771
TF	0	04	1005-2450	73004	2		12.39	2730	5853	1875	770	897	155	40	26	1120	27	94	910	20	1609
TF	1	04	1005-2450	73003	2		12.39	782	558	1961	4241	4215	451	416	15	115	25	61	337	44	1299
TF	0	07	0103-0815	73006	2		6.05	2055	3544	1344	4995	493	111	36	74	792	36	109	340	14	1200
TF	1	07	0103-0815	73005	2		6.05	41543	10791	1306	4995	4941	4105	433	31	94	42	78	315	413	1140
TF	0	07	0815-1400	73053	2		6.51	2961	4822	870	1818	1096	108	33	45	1420	62	175	364	412	1840
TF	1	07	0815-1400	73052	2		6.51	41951	10114	647	4959	4904	498	431	423	137	63	101	267	412	1400

TABLE A1. (CONT.) LD VOL DATA

SITE	SIZE	DATE	TIME	INT.	ID	NOTE	VOLUME	AL	SI	S	K	CA	TI	V	MM	FE	CU	ZN	BR	SR	PM
TF	0	07	1600-2355	73060	2		6.65	<1079	2291	<632	<499	<401	<56	<30	24	398	38	<12	157	<12	495
TF	1	07	1600-2355	73059	2		6.65	<1079	<493	<632	<499	<401	<56	<30	<23	<30	47	<12	132	<12	377
TF	0	09	0000-0820	73070	2		7.00	3588	3482	9105	<428	522	<52	<29	27	693	49	90	339	24	945
TF	1	09	0000-0820	73069	0		7.00	<1595	11290	1916	<390	<381	<42	31	23	269	31	42	122	<11	715
TF	0	09	0825-2356	73063	2		13.06	2681	9129	9252	916	539	48	<15	12	726	26	43	392	19	1900
TF	1	09	0825-2356	73064	0		13.06	1997	7322	3292	237	<221	<49	<15	<11	329	24	24	344	<6	1150
TF	1	19	0000-0816	73108	2		6.97	1939	2112	<626	<391	<419	<64	35	37	901	49	54	710	<11	2060
TF	0	19	0830-3710	73103	2		29.08	1379	2933	348	345	478	64	9	19	564	14	72	120	5	545
TF	1	19	0830-3710	73118	2		29.08	627	903	308	<113	<119	<23	<6	9	187	19	30	110	<3	491
TF	0	16	0000-0800	73121	2		6.72	9020	7951	709	1012	1179	194	<30	74	1549	56	151	929	18	1290
TF	1	16	0000-0800	73126	2		6.72	2049	877	<650	496	<430	<67	<30	43	585	32	142	368	<12	1070
TF	0	16	0810-2401	73113	2		13.31	6499	1953	938	1876	1975	254	21	68	479	37	106	754	25	2360
TF	1	16	0810-2401	73136	1		13.31	2390	9016	<328	558	535	76	<15	32	704	21	64	837	9	1959
TF	0	17	0023-1648	73111	2		13.79	9363	8694	924	987	1679	137	20	65	1620	32	176	844	13	2790
TF	1	17	0023-1648	73134	2		13.79	2795	3677	966	531	565	71	<14	56	755	43	153	829	8	2610
TF	0	21	0000-0909	73105	2,3		6.85	<1631	<4964	<637	<398	<422	<55	<29	<22	165	46	17	291	<11	707
TF	1	21	0000-0909	73164	2,3		6.85	<1631	1533	2172	<398	<422	<55	<29	53	337	32	116	454	<11	1390
TF	0	21	0800-1750	73149	2		6.13	9156	7951	3225	938	1455	147	39	48	189	39	58	285	34	1269
TF	1	21	0812-1750	73158	2		6.09	1977	2967	2946	935	374	83	<25	20	526	39	39	207	15	1070
WB	0	07	0200-0830	73015	2		5.46	3384	5983	1189	557	790	146	<37	85	1189	56	191	585	22	1879
WB	1	07	0200-0830	73013	2		5.46	<2047	<1409	914	<500	<529	<108	<37	<28	9	90	139	469	<15	1629
WB	0	07	0830-1636	73058	2		6.72	9520	8691	820	1115	1375	141	<30	59	1230	74	156	315	18	1739
WB	1	07	0830-1636	73055	2		6.72	<1663	<4983	<650	<406	<430	<67	<30	24	184	89	85	217	<12	1239
WB	0	07	1440-2325	73058	2		5.67	<1970	3612	<770	<491	<509	<104	<36	<27	644	36	15	185	<14	616
WB	1	07	1440-2325	73057	2		5.67	<1970	<1166	<770	<491	<509	<104	<36	<27	<36	36	<14	140	<14	431
WB	0	09	0010-0800	73064	2		6.58	6999	8191	8436	847	1898	242	92	138	1870	61	92	443	85	1670
WB	1	09	0010-0800	73065	0		6.58	<1497	<1604	3280	<414	<438	<69	33	40	106	57	76	226	<12	906
WB	0	09	0810-2430	73072	2		13.72	5202	9191	4545	1120	1476	212	23	38	1790	23	66	513	50	2210
WB	1	09	0810-2430	73071	0		13.72	2585	4532	5280	365	221	71	20	31	510	25	36	585	6	1620
GM	0	17	0000-0800	73193	2		6.72	7679	15290	766	2065	2729	260	66	110	3740	56	482	978	32	3120
GM	1	17	0000-0800	73192	2		6.72	<1663	<4983	<650	<406	<430	<67	<30	40	198	32	335	806	<12	2400
GM	0	17	0900-1600	73191	2		5.88	3045	7225	<742	743	1072	144	<34	45	1340	91	75	112	15	598
GM	1	17	0900-1600	73198	2		5.88	<1899	<1124	<742	<464	<491	<100	<34	<24	1459	43	52	357	18	1230
GM	0	17	1612-2400	73179	2		6.55	2815	6808	4646	820	1088	114	<31	29	1459	43	52	357	18	1230
GM	1	17	1612-2400	73146	2		6.55	<1706	<1008	4666	<416	<441	<69	<31	<23	<31	33	<12	285	<12	969
GM	0	21	0000-0800	73189	2		6.72	5906	13419	2053	1698	1616	251	<30	50	3020	91	212	495	18	1640
GM	1	21	0000-0800	73186	2		6.72	3181	6579	6650	785	974	134	<30	24	1239	41	70	500	13	1920
GM	0	21	0925-1700	73177	2		6.37	7436	14998	5452	2021	2139	242	40	100	2689	74	228	359	90	1920
GM	0	21	1710-2430	73187	2		6.16	5954	12966	809	2078	2122	212	42	58	1939	61	71	419	14	1989
GM	1	21	1710-2430	73150	2		6.16	<1813	<1072	<709	<486	<433	<495	<33	<24	<24	30	15	467	<13	1409

TABLE A2 CORRELATION COEFFICIENTS • 1000 FOR LO VOL DATA (NO SIZE FRACTIONATION)

	AL	SI	S	K	CA	TI	MN	FE	CU	ZN	BR	PB
AL	1000	943	281	905	925	937	740	955	617	744	756	814
SI	943	1000	51	982	892	923	661	975	552	691	790	837
S	281	51	1000	183	358	433	226	97	392	-33	-124	-22
K	905	982	183	1000	839	891	589	932	520	646	760	800
CA	925	892	358	839	1000	941	709	937	834	696	615	728
TI	937	923	433	891	941	1000	733	952	754	715	678	775
MN	740	661	226	589	709	733	1000	735	596	733	577	631
FE	955	975	97	932	937	952	735	1000	594	772	778	828
CU	517	552	392	520	834	754	596	594	1000	466	303	458
ZN	744	691	-33	646	696	715	733	772	466	1000	798	825
BR	756	790	-124	760	615	678	577	778	303	798	1000	966
PB	814	837	-22	800	728	775	631	828	458	825	966	1000

TABLE A 3 INTERCEPTS / SLOPES FROM LINEAR REGRESSION ANALYSIS FOR LO VOL DATA (NO SIZE FRACTIONATION)

	AL	SI	S	K	CA	TI	MN	FE	CU	ZN	BR	PB
AL	.000	.557+03	.392+04	.839+03	.155+04	.875+03	.143+04	.824+03	.321+04	.224+04	.181+04	.146+04
	.100+01	.434+00	.262+00	.302+01	.210+01	.191+02	.512+02	.204+01	.184+02	.146+02	.517+01	.155+01
SI	-.177+03	.000	.875+04	.636+03	.509+04	.154+04	.294+04	.780+03	.569+04	.381+04	.259+04	.203+04
	.205+01	.100+01	.105+00	.702+01	.432+01	.402+02	.100+03	.458+01	.384+02	.308+02	.120+02	.349+01
S	.156+04	.275+04	.000	.180+04	.150+04	.791+03	.177+04	.258+04	.219+04	.309+04	.349+04	.307+04
	.301+00	.247+01	.100+01	.583+00	.815+00	.824+01	.163+02	.216+00	.118+02	.708+00	.931+00	.476+01
K	.279+01	-.435+02	.123+04	.000	.428+03	.210+03	.517+03	.141+03	.948+03	.665+03	.468+03	.382+03
	.271+00	.137+00	.571+01	.100+01	.570+00	.539+01	.122+02	.597+00	.446+01	.373+01	.151+01	.441+00
CA	-.424+03	-.273+03	.117+04	-.730+02	.000	-.217+03	.124+03	-.203+03	.783+03	.563+03	.494+03	.264+03
	.407+00	.184+00	.157+00	.123+01	.100+01	.853+01	.216+02	.892+00	.104+02	.585+01	.183+01	.600+00
TI	-.150+02	.210+01	.159+03	.123+02	.461+02	.000	.453+02	.824+01	.140+03	.983+02	.826+02	.586+02
	.459+01	.212+01	.228+01	.147+00	.104+00	.100+01	.254+01	.101+00	.101+01	.664+00	.224+00	.709+01
MN	.125+02	.207+02	.556+02	.263+02	.285+02	.202+02	.000	.200+02	.439+02	.274+02	.303+02	.260+02
	.107+01	.436+02	.314+02	.284+01	.232+01	.212+00	.100+01	.225+01	.252+00	.211+00	.575+01	.174+01
FE	-.218+03	-.844+02	.170+04	.349+02	.424+03	.108+03	.330+03	.000	.100+04	.537+03	.395+03	.268+03
	.446+00	.208+00	.436+01	.145+01	.985+00	.898+01	.240+02	.100+01	.881+01	.742+01	.254+01	.744+00
CU	-.286+02	.424+01	.277+02	.110+02	.329+02	.511+02	.220+02	.909+00	.000	.192+02	.310+02	.138+02
	.207+01	.793+02	.130+01	.806+01	.666+01	.563+00	.141+01	.401+01	.100+01	.305+00	.666+01	.276+01
ZN	.211+02	.112+02	.171+03	.141+02	.310+02	.313+01	.269+01	.116+02	.939+02	.000	.145+02	.428+01
	.380+01	.155+01	.159+02	.112+00	.827+01	.770+00	.254+01	.802+01	.712+00	.100+01	.270+00	.769+01
BR	.995+01	.297+02	.604+03	.347+02	.221+03	.164+03	.164+03	.800+02	.363+03	.128+03	.000	-.446+01
	.111+00	.522+01	.169+01	.383+00	.206+00	.206+01	.579+01	.238+00	.138+01	.236+01	.100+01	.266+00
PB	.381+01	.907+02	.213+04	.140+03	.691+03	.332+03	.564+03	.280+03	.124+04	.506+03	.127+03	.000
	.428+00	.201+00	.112+01	.145+01	.882+00	.846+01	.229+02	.922+00	.758+01	.885+01	.351+01	.100+01

TABLE A4 TWO HOUR AVERAGES (NO SIZE FRACTIONATION)

SITE	SIZE	DAY	TIME	INT	AL	SI	S	K	CA	TI	MN	FE	*	ZN	BR	PB	MSPO	MSCAT	CO
TF	U	6	0100-0300		4431.	4950.	6932.	570.	569.	157.	90.	1109.	7146.	250.	1129.	3680.	9.20	10.60	
TF	U	6	0300-0500		2795.	2901.	3323.		490.		77.	748.	3554.	370.	583.	1890.			
TF	U	6	0500-0700			1146.	1398.				34.	346.	1546.	315.	250.	847.			
TF	U	6	0700-0900			1677.	948.				34.	418.	2303.	180.	587.	1829.			
TF	U	6	0900-1100		2102.	2494.	3533.		456.	117.	28.	480.	3276.	82.	353.	1510.			
TF	U	6	1100-1300		2363.	2546.	3225.		473.	123.	34.	509.	2581.	61.	208.	965.			
TF	U	6	1300-1500		2634.	3079.	2676.		509.			583.	2408.	44.	296.	1069.			
TF	U	6	1500-1700		2172.	2306.	2573.				46.	804.	2213.	57.	707.	2080.			
TF	U	6	1700-1900		3588.	4677.	2266.	534.	656.	117.	51.	928.	3412.	110.	846.	2680.			
TF	U	6	1900-2100		4270.	5353.	1465.	571.	728.			521.	2124.	143.	489.	1627.			
TF	U	6	2100-2300		2099.	2741.	990.					473.	1802.	41.	246.	843.	6.20	3.20	
TF	U	7	0100-0300			2046.	1918.				125.	453.	2500.	164.	412.	1420.			
TF	U	7	0300-0500		1963.	2496.	2160.		509.	110.		394.	1291.	89.	246.	773.			
TF	U	7	0500-0700			1496.	1036.				43.	1109.	3002.	176.	831.	2469.			
TF	U	7	0700-0900		3409.	4708.	1068.	552.	695.	184.	28.	2149.	4875.	340.	1015.	4265.			
TF	U	7	0900-1100		6111.	9967.	1212.	1168.	1603.			418.	1261.	57.	187.	859.	3.40	2.90	
TF	U	7	1100-1300			1758.	805.					237.	605.	20.	34.	221.			
TF	U	7	1300-1500				768.					196.	488.	23.	118.				
TF	U	7	1500-1700									254.	1032.	267.	662.				
TF	U	7	1700-1900																
TF	U	7	1900-2100																
TF	U	7	2100-2300																
TF	U	9	0700-0900																
TF	U	9	0900-1100		4545.	3385.	16398.		577.			526.	4692.	32.	105.	493.	2.80	4.17	2.90
TF	U	9	1100-1300			2496.	10038.					372.	5372.	27.	73.	353.	7.10	5.18	2.09
TF	U	9	1300-1500		3431.							381.	4210.	20.	331.	810.	8.90	5.18	.96
TF	U	9	1500-1700		2863.	2595.	6600.		636.	115.		429.	2226.	48.	1209.	2849.	6.80	4.18	.69
TF	U	9	1700-1900		4661.	4516.	8758.					284.	4355.	23.	600.	1469.			
TF	U	9	1900-2100		2747.	1903.	5772.												
TF	U	10	0100-0300																
TF	U	10	0300-0500																
TF	U	10	0500-0700																
TF	U	10	0700-0900																
TF	U	10	0900-1100																
TF	U	10	1100-1300																
TF	U	10	1300-1500																
TF	U	10	1500-1700																
TF	U	10	1700-1900																
TF	U	10	1900-2100																
TF	U	10	2100-2300																
TF	U	14	0300-0500																
TF	U	14	0500-0700																
TF	U	14	0700-0900																
TF	U	14	0900-1100		4181.	5677.	1933.	736.	1021.	123.	55.	1230.	2636.	143.	418.	1670.	2.90	3.93	8.37
TF	U	14	1100-1300																
TF	U	14	1300-1500																
TF	U	14	1500-1700																
TF	U	14	1700-1900																
TF	U	14	1900-2100																
TF	U	14	2100-2300		9090.	15431.													
TF	U	16	0100-0300		7770.	12372.													
TF	U	16	0300-0500		4270.	6625.	1021.												
TF	U	16	0500-0700		3545.	5664.													
TF	U	16	0700-0900		6406.	10607.	1138.												
TF	U	16	0900-1100		3202.	6445.	2798.												
TF	U	16	1100-1300			1917.													
TF	U	16	1300-1500			2174.													
TF	U	16	1500-1700			2664.													
TF	U	16	1700-1900																
TF	U	16	1900-2100		9090.	15431.													
TF	U	16	2100-2300		7770.	12372.													
TF	U	17	0100-0300		4270.	6625.	1021.												
TF	U	17	0300-0500		3545.	5664.													
TF	U	17	0500-0700		6406.	10607.	1138.												
TF	U	17	0700-0900		3202.	6445.	2798.												
TF	U	17	0900-1100			1917.													
TF	U	17	1100-1300			2174.													
TF	U	17	1300-1500			2664.													
TF	U	17	1500-1700																

* = (PB) + 1/2(S)

TABLE AS CORRELATION COEFFICIENTS • 1000 FOR TWO HOUR AVERAGES (NO SIZE FRACTIONATION)

	AL	SI	S	K	CA	TI	MN	FE	•	ZN	BR	PB	WSPD	BSCAT	CO
AL	1000	939	110	959	761	888	38	866	634	484	854	863	-583	177	
SI	939	1000	-96	978	830	907	290	960	545	508	871	891	-489	208	936
S	110	-96	1000		-261	-178	289	-151	810	-272	-82	-106	-67	478	
K	959	978		1000	763		88	951	574	590	714	805			
CA	761	830	-261	763	1000	798	57	878	307	458	624	695	-539	-185	
TI	888	907	-178		798	1000	-168	862	614	549	860	874			
MN	38	290	289	88	57	-168	1000	322	257	415	90	150			
FE	866	960	-151	951	878	862	322	1000	549	648	842	907	-541	237	935
•	634	545	810	574	307	614	257	549	1000	282	620	644	-326	674	535
ZN	484	508	-272	590	458	549	415	646	282	1000	519	625	-456	318	806
BR	854	871	-82	714	624	860	90	842	620	519	1000	973	-445	358	952
PB	863	891	-106	805	695	874	150	907	644	625	973	1000	-488	403	972
WSPD	-583	-489	-67		-539			-541	-326	-456	-445	-488	1000	-85	-488
BSCAT	177	208	478		-185			237	674	318	358	403	-85	1000	354
CO		936						935	535	806	952	972	-488	354	1000

* = (PB) + 1/2(S)

TABLE A6 INTERCEPTS / SLOPES FROM LINEAR REGRESSION ANALYSIS FOR TWO HOUR AVERAGES (NO SIZE FRACTIONATION)

	AL	SI	S	K	CA	TI	MN	FE	*	ZN	BR	PB	WSPD	BSCAT	CO
AL	.000	.136+04	.334+04	.773+03	.119+04	.171+04	.417+04	.152+04	.277+04	.207+04	.169+04	.836+04	.420+04		
	.100+01	.490+00	.375+01	.514+01	.366+01	.425+02	.175+01	.278+01	.602+00	.814+01	.238+01	.993+00	.564+03	.144+03	
SI	-.184+04	.000	.394+04	.344+03	.404+03	.569+04	.384+04	.31+03	.145+04	.235+04	.137+04	.782+03	.934+04	.446+04	.242+04
	.180+01	.100+01	.660+01	.983+01	.756+01	.827+02	.263+02	.587+01	.876+00	.161+02	.473+01	.194+01	.502+03	.342+03	.116+04
S	.274+04	.372+04	.000		.518+04	.430+04	.158+04	.393+04	.129+04	.440+04	.344+04	.361+04	.444+04	.798+03	
	.323+00	.141+00	.100+01		-.247+01	.103+02	.465+01	.116+01	.142+01	.905+01	.664+00	.319+00	.732+02	.866+03	
K	-.712+02	.684+02		.000	.199+03		.799+03	.112+03	.264+03	.344+03	.380+03	.179+03			
	.178+00	.974+01		.100+01	.626+00		.655+00	.672+00	.131+00	.245+01	.373+00	.192+00			
CA	.148+03	.262+03	.646+03	.231+03	.000	-.302+03	.823+03	.176+03	.574+03	.547+03	.506+03	.406+03	.133+04	.105+04	
	.158+00	.910+01	.276+01	.929+00	.100+01	.813+01	.552+00	.607+00	.569+01	.167+01	.352+00	.164+00	.532+02	.310+02	
TI	.636+02	.830+02	.145+03		.775+02	.000	.167+03	.782+02	.892+02	.103+03	.100+03	.866+02			
	.186+01	.994+02	.310+02		.784+01	.100+01	.159+00	.602+01	.145+01	.272+00	.506+01	.221+01			
M	.669+02	.467+02	.450+02	.653+02	.553+02	.108+03	.000	.399+02	.415+02	.323+02	.597+02	.543+02			
	.831+03	.319+02	.666+02	.119+01	.597+02	.179+00	.100+01	.235+01	.662+02	.175+00	.575+02	.407+02			
FE	-.120+03	.110+03	.700+03	.282+03	.644+01	.666+03	.756+03	.000	.310+03	.361+03	.311+03	.197+03	.166+04	.774+03	.422+03
	.270+00	.157+00	.200+01	.135+01	.127+01	.123+02	.442+01	.100+01	.143+00	.332+01	.752+00	.323+00	.912+02	.637+02	.198+03
*	.129+04	.169+04	.167+04	.219+04	.245+04	.224+03	.281+04	.142+04	.000	.269+04	.177+04	.181+04	.502+04	.111+04	.189+04
	.668+00	.339+00	.464+00	.252+01	.166+01	.260+02	.100+02	.211+01	.100+01	.537+01	.213+01	.881+00	.21+03	.708+03	.518+03
ZN	.208+02	.555+02	.150+03	.778+02	.509+02	.946+01	.120+03	.228+02	.743+02	.000	.671+02	.424+02	.310+03	.875+02	.385+03
	.288+01	.161+01	.625+02	.142+00	.125+00	.111+01	.984+00	.127+00	.148+01	.100+01	.898+01	.438+01	.270+02	.143+02	.291+02
BR	-.433+03	.770+02	.525+03	.583+02	.700+02	.132+04	.730+03	.129+03	.261+02	.249+03	.000	-.827+02	.138+04	.322+03	.161+02
	.306+00	.160+00	.103+01	.137+01	.110+01	.146+02	.140+01	.942+00	.180+00	.500+01	.100+01	.388+00	.909+02	.117+03	.283+03
PB	-.714+03	.390+02	.167+04	.572+03	.745+01	.233+04	.211+04	.207+03	.266+03	.731+03	.270+03	.000	.388+04	.942+03	.150+03
	.750+00	.410+00	.362+01	.337+01	.295+01	.346+02	.552+01	.255+01	.470+00	.844+01	.244+01	.100+01	.249+03	.329+03	.676+03
WSPD	.926+01	.102+02	.669+01		.126+02		.107+02	.921+01	.748+01	.904+01	.944+01	.000	.447+01	.781+01	
	-.606+03	.478+03	.624+04		-.548+02		-.322+02	-.499+03	.773+02	.219+02	.959+03	.100+01	.142+00	.645+00	
BSCAT	.287+01	.254+01	.248+01		.466+01		.239+01	.106+01	.246+01	.248+01	.225+01	.319+01	.000	.202+01	
	.218+03	.127+03	.264+03		-.112+02		.679+03	.642+03	.706+02	.110+02	.494+03	.515+01	.100+01	.287+00	
CO		-.156+01					-.160+01	.449+00	.129+01	.248+00	.939+01	.489+01	.107+01	.000	
		.754+03					.441+02	.551+03	.223+01	.320+02	.140+02	.371+00	.604+00	.100+01	

* = (PB) + 1/2(S)

AN ANALYSIS OF PARTICULATES FROM THE DENVER URBAN PLUME
USING SCANNING ELECTRON MICROSCOPY AND ENERGY
DISPERSIVE X-RAY SPECTROMETRY

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ABSTRACT

Millipore substrates and backup filter of an Anderson 8-stage impactor operated at the Trout Farm sampling site on 16 November 1973 were intensively examined using scanning electron microscopy and X-ray energy dispersive spectroscopy. Impactor stages from the Trout Farm sampling site for 14, 17 and 21 November 1973 and Adams County Fair-ground sampling site 14, 16 and 21 November 1973 were also examined. It was determined that there was little or no significant difference in particle size distribution across the substrates or backup filter of the Anderson impactors. However, there was large variation of particle sizes on any stage and the pattern of size deposition on progressive stages was species dependent. Large mineral particles were predominant in the initial stages of the impactor while auto emission products and sulfur were observed mainly on the last stages. Flyash was observed in all stages. Most flyash produced X-ray fluorescence spectra very similar to major mineral components of Denver's plume. Particles greater than one micrometer made up the great bulk of the particulates samples; they were almost entirely mineral with clay, potassium aluminum silicates and quartz predominating. Particles less than one micrometer were predominantly auto emission and mineral or mineral-like material. The estimated concentration of particles greater than one micrometer was $1.55 \times 10^6/\text{m}^3$, less than one micrometer was $5.89 \times 10^9/\text{m}^3$. Sulfur was predominantly associated with the smallest particulates, auto emission; its source, however, was not automotive.

INTRODUCTION

A major portion of urban air pollution is composed of particulates which are products of (1) natural erosion entrained by wind or volcanic activities (fugitive dust), (2) natural erosion entrained by man's activities (automotive, farming, building and industrial activities), (3) combustive processes which are primarily associated with power plants and heavy industry, and (4) auto emissions. The last two categories contribute metals to the atmosphere in concentrations greater than the crustal composition (van Valin 1974 and Duce 1975); this contribution is observed world wide and is assumed to contribute about 2.5% to earth's total aerosol mass, although the contribution can be as great as 500% of naturally produced aerosols near the source of production (Research/Development, News Notes August 1974).

Knowledge of size distribution and composition of particulates that are in the environment of men is a very important health concern because the lungs act as a selective filter, capturing particles less than 1 μm in diameter (Natusch 1974). This is particularly important as some toxic metals and organic compounds are found in relatively high concentrations in respirable particles (Loh 1974, Natusch 1974, and Davison 1974). In the lungs, extraction of toxic material can be as high as 60% to 80% (Davison 1974). Even relatively inert materials may be harmful if they are deposited in the lungs, i.e., freshly dry-crushed quartz (Hanusiak 1975). Particles less than 1.0 μm are also responsible for visible light scattering which contributes very significantly to reduction in visibility (O'Brien 1974).

The Environmental Protection Agency invited the Denver Research Institute, University of Denver, to participate in the 1973 Field Study of the Denver "Brown Cloud" and, as a part of its contribution, to use scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS) analysis to characterize particulates collected on an Anderson 8-stage impact sampler. The SEM-EDS study was to (1) obtain an estimate of the particulate composition of the Denver plume, (2) evaluate the need for a fine particulate ambient air standard and (3) determine the effectiveness of the 8-stage Anderson impactor using Millipore substrates.

METHODS AND MATERIALS

The 0.8 μm Millipore backup filter and stage substrates from the Anderson 8-stage sampler operated on 16 November 1973 at the Trout Farm sampling location were selected for intensive examination to (1) obtain particulate information of the Denver Urban Plume and (2) determine the effectiveness of the Anderson impactor using Millipore substrate.

Pie-shaped segments (approximately 20°) were cut from the backup filter with each of the eight samples including portions from the center

to outer edge; the sections were attached to an appropriately sized piece of clean Plexiglass which was attached to an SEM stub. The attached substrate was then vacuum coated with approximately 200Å of carbon.

Particulates in outer, middle and center portions of each stage and the backup filter were examined in a scanning electron microscope for morphology and chemically characterized using an energy dispersive X-ray spectrometer. All examinations were conducted using a 30 KeV accelerating potential, 45° specimen tilt angle and 15° specimen rotation.

For the backup filter and stage 0, 1 and 2 particles were dispersed enough on the substrate to allow relatively easy in situ examination. The procedure was to examine a portion of each segment at 1000X or 2000X magnification and take a photograph which was subsequently divided into quadrants. These were then examined thoroughly at higher magnifications. Photographs were taken at high enough magnifications to allow size measurements and morphological observations. Size was measured from the photograph and converted to effective diameter in μm . For non-spherical particles this was derived from the mean of two measurements taken at right angles to a line through the particle's longest axis. Each particle was X-ray analyzed for 100,000 total counts, all elemental peaks were quantified for integrated counts and the spectrum plotted for future reference. An optimum sample size of 30 particles was selected for each portion of a segment; this figure was usually exceeded.

Stages 3-7 presented a problem as particle distribution became progressively more dense, producing a spot of concentrated material. Extensive efforts were made to representatively redistribute the particles on an inert substrate; satisfactory results were not obtained. (We later concluded that the substrate filters were probably composed of Millipore Celatate which is impervious to most solvents). It was assumed that particulates observed outside but near the compact spots would be representative of particulates impacted on each substrate. Observations of gross spot X-ray analyses suggested this was true, except for stages 6 and 7. The X-ray analysis procedure was also modified to permit more rapid chemical classification of particles. The collection of X-ray information from a particle was continued until the strongest peaks were clearly evident (20,000 to 50,000 total counts) and then elements were recorded as major, moderate or trace. Major compositional elements were those that had an integrated peak height greater than background including peaks that were $\geq 50\%$ of the strongest peak's height; moderate elements also had a well-defined emission peak but one that was less than 50% the height of the strongest element present; trace elements had poorly defined peaks with heights only slightly above background. The charts produced for the backup filter and impact substrates 0-2 were also examined in this manner so that their particulate data could be compared with the later stages. With the help of a particle atlas (McCrone 1973) and mineral/chemical standards prepared in our laboratory, particles were assigned to the various categories (Table 1). Distinctive morphology was also noted and used as an aid in determining particle species.

Table 1

Particle Classification, Energy Dispersive Spectrometry (30 KeV),
for the Denver Urban Plume Study

Type	Elemental Composition	
	Major	Moderate
<u>Mineral</u>		
Quartz	Si	(Fe) ¹
Aluminum silicates		
Clay	Si	Al,(K,Ca),(Fe)
Potassium	Si	Al,K,(Fe)
Calcium	Si	Al,Ca,(Fe)
Iron	Si,(Fe)	Al,Fe
Calcium	Ca	(Fe),(Si)
Calcium/sulfur	Ca,S	--
Rutile	Ti	(Si),(Al),(K),(Ca)
<u>Flyash</u>		
Si-rich	Si	Al,K,Ca,(Fe),(Ti)
Ca-rich	Ca,(Si)	(Al),(Si),(K),(Fe),(Ti)
Metal-rich	(Pb),(Fe),(Si)	(Si),(K),(Ca),(Ti)
<u>Lead Rich</u>		
Lead bromochloride	Pb	Cl,Br
Lead	Pb	--
<u>Metals</u>	Various	--
<u>Salts</u>	Various	--
<u>Carbon</u>		
Particle	--	(K)(Ca),(Si),(Al),(S)
Auto emission	--	(Pb),(Cl),(Br),(S)
Spheres	--	--

¹() - sometimes present

For comparative purposes, total impact spots from various stages and samples were examined using EDS. For each examination the SEM-EDS parameters were identical to those of the detailed particulate examination. Stages 3 through 7 were examined for the Trout Farm (Nov. 14, 16, 17, 21) and Adams County Fairground (Nov. 14, 16, 21) sampling locations. The impaction media for the Trout Farm samples was Millipore filter, while that of the Adams County Fairground was Nuclepore filter.

RESULTS

I. Observation of Particle Size Discrimination by the 16 November Trout Farm Anderson 8-Stage Impactor Using Millipore Substrates and Backup Filter

The effective mean diameters, chemical composition and particle classification for each stage and radial location are presented in Appendix Tables 1-27; summaries of particle sizes are presented in Appendix Tables 28-43. The diameters of mineral and flyash particles for the various impactor stages and the backup filter are presented in Figures 1 and 2, the vertical lines display the standard deviation of all the specified particle types observed on any one stage. Because of particle compaction and the lack of distinguishable particles, stage 7 was not examined for mineral or flyash particles near the impact spot (this will be discussed later).

The variance of diameters of minerals and flyash collected on each stage was examined by comparing the mean diameter of all flyash or mineral particles on a stage with particles sampled from outer, middle and center locations on the impact media. Only twice was there a difference between a stage's specified particle type mean diameter and the mean diameter at the center, middle or outer portion when tested at the 5% significance level: (1) flyash particles from the outer portion of stage 6 and (2) mineral particles from the center portion of stage 2.

II. Particulate Composition of the Urban Plume at the Trout Farm, 16 November 1973

For the backup filter and impact stages 0-5 the examination was relatively simple. Figure 3 illustrates two different types of flyash particles and a lead particle; the association of particles at the bottom are typical mineral type particles, in this example all were clay. The two types of flyash in the figure are representative of the majority of flyash encountered: (1) the Si-rich type which is virtually indistinguishable from mineral clay except by spherical morphology; and (2) the Ca-rich type which characteristically exhibited a strong calcium X-ray peak with other variable elemental peaks (note association with auto emission). Figures 4a and b are examples of auto emission particles found on various stages of the Anderson impactor. Figure 4c is an

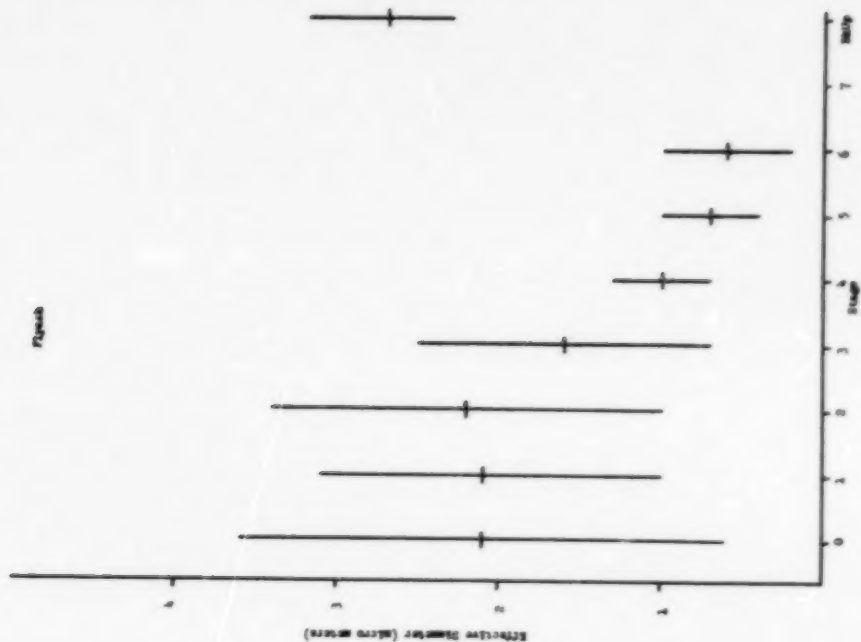


Fig. 1. Mean effective diameter of mineral particles collected on the various stages of an Anderson Impactor, Trout Farm Sampling Site, 16 Nov. 1973

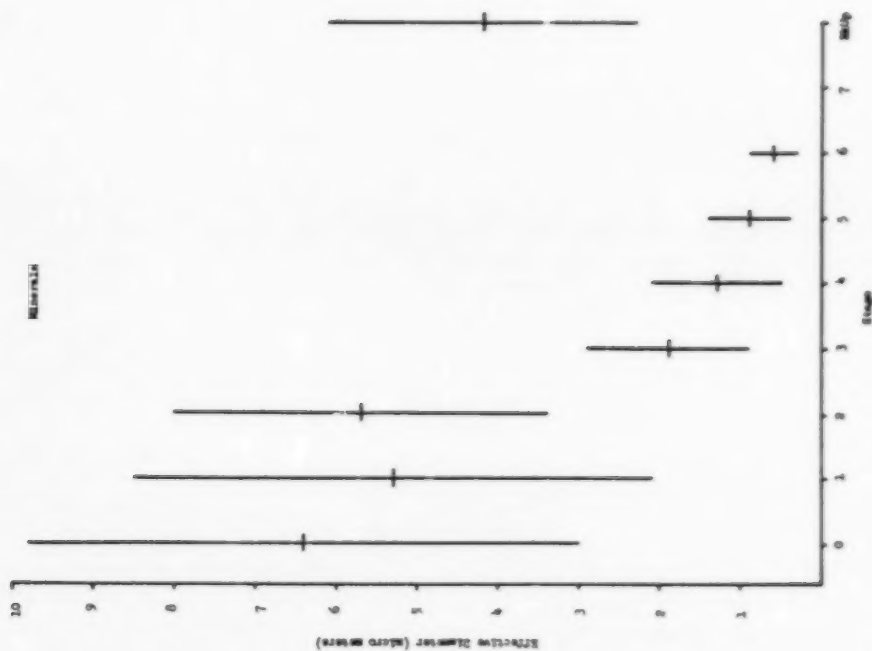
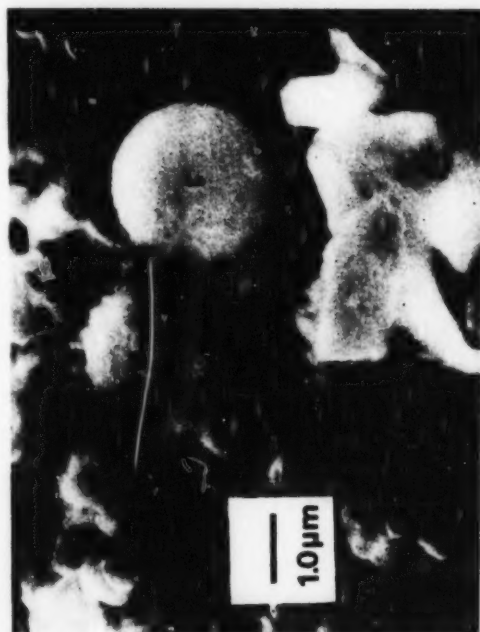


Fig. 2. Mean effective diameter of flyash particles collected on the various stages of an Anderson Impactor, Trout Farm Sampling Site, 16 Nov. 1973



Particle A X-ray spectra (Metallic Lead)



Particle C X-ray spectra (flyash, Ca rich)



Particle B X-ray spectra (flyash, Si rich)

Figure 3. Representative particles with X-ray spectra from stage 3 of the Trout Farm Anderson 8-stage impactor, 16 Nov. 1973.



Fig. 4a



Fig. 4b



Fig. 4c

Figure 4. Representative Particles of Auto Emission from the Trout Farm Anderson 8-stage Impactor, 16 Nov. 1973.

example of an EDS analysis of a particle like 4a; in many cases no characteristic elemental X-ray peaks were observable. In the last three stages (5-7) independent particles and particles embedded in auto emission produced emission lines for lead, chlorine and bromine. These particles were assumed to be lead bromochloride. Figure 5 compares standards of lead bromide (PbBr_2) and lead chloride (PbCl_2) with a particle of lead bromochloride found on an impactor substrate. The particle produced a fluorescence pattern that was most similar to the PbCl_2 pattern.

Appendix Table 44 presents the X-ray spectroscopy of the various impact spots for stages 3-7, Figure 6 illustrates the X-ray spectra from which these data were derived (the spectra from stage 3 is omitted because it is very similar to that of stage 4). The Al/Br fluorescence line can be produced by aluminum K_α or bromine L_α emission and the S/Pb fluorescence line can be produced by sulfur K_α or lead M_α emission. When the data are reduced (Appendix Tables 45, 46, and 48a), it is obvious that the relative amount of silicon containing material is progressively reduced from stage 3-7 while the amount of lead and/or sulfur is increased. By observing the lead L_α intensity it is apparent that lead is most prevalent in stage 5 while sulfur becomes a major component in stages 6 and 7 (Figure 7). It is noteworthy that while individual particles of lead and lead bromochloride were observed, no particles containing primarily sulfur were detected.

By comparing the fluorescence patterns of stage 6 (Appendix Table 48a) with the particles observed (Appendix Tables 34 and 42), it was obvious that the particles around the compact impact spots for the later stages were not representative of the spots themselves. Close examination of spots on stages 6 and 7 revealed that the spots were made up of two distinct regions; the inner area of the middle spot of Stages 6 and 7 exhibited stronger emission for the elements of S, Pb, Br and Zn (Appendix Tables 45 and 46). Particles in the inner area had a mean diameter of $0.28 \pm 0.15 \mu\text{m}$ and were rounded but not spherical in shape, while the particles in the outer area were $0.08 \pm 0.03 \mu\text{m}$ in mean diameter with a morphology similar to carbon black samples which have been examined previously by DRI's microscopy laboratory.

Using the silicon emission peak's percent of total integrated counts for each spot (Appendix Table 48a) and comparing it with the volume-percent of minerals for stages 3, 4 and 5 (Appendix Table 51), a linear regression was observed with a correlation coefficient of 0.97. From this regression the percent-volume mineral composition of stages 6 and 7 was estimated at 68.6 and 64.4 percent, respectively.

III. Estimate of Particulate Size Distribution

An estimate of the number of particles collected on the Anderson

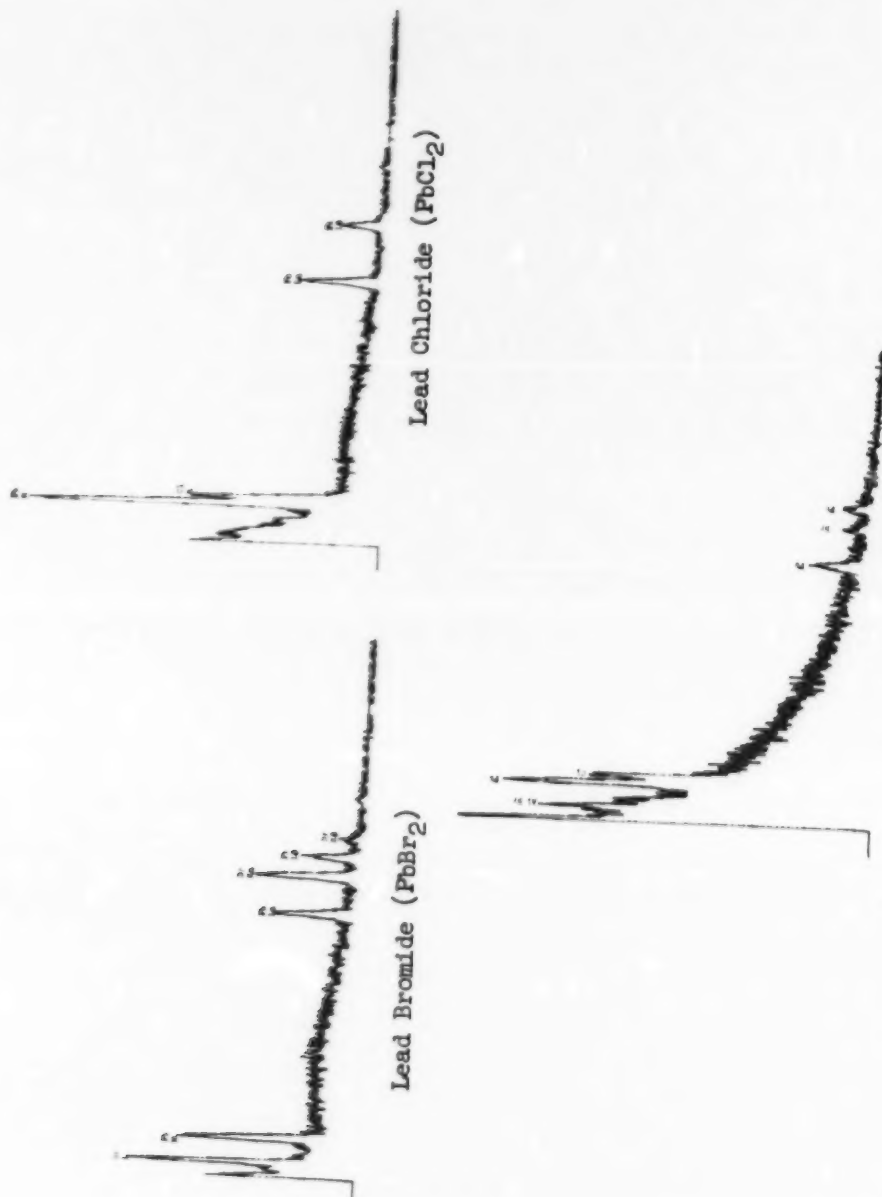
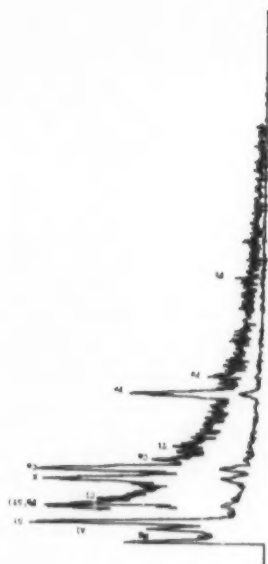


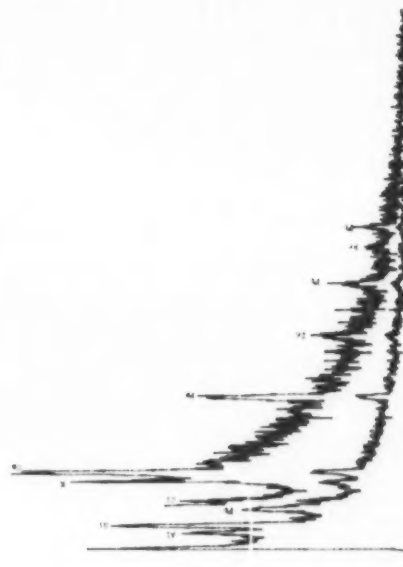
Figure 5. X-ray energy dispersive spectrometry of lead bromide (PbBr₂), lead chloride (PbCl₂) and lead bromochloride observed on the Trout Farm Anderson impactor, 16 Nov. 1973.



Stage 5



Stage 4



Stage 6



Stage 7

Figure 6. X-ray spectroscopy of stage 4-7 impacted material, Anderson 8-stage impactor, Trout Farm sampling site, 16 Nov. 1973.

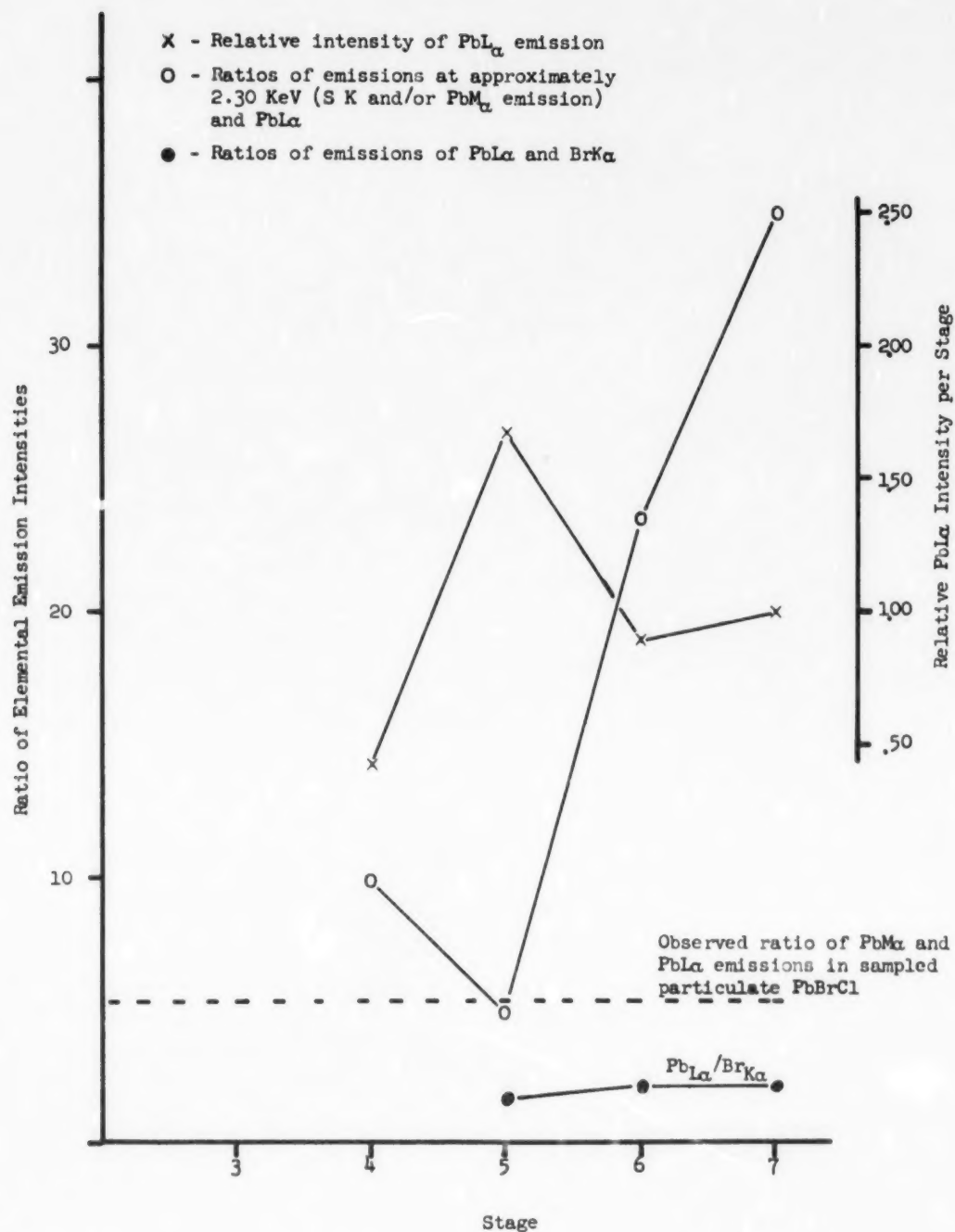


Fig. 7. Comparison by stage of the Trout Farm Anderson impactor, 16 Nov. 1973, for sulfur and lead X-ray emissions.

impactor was made using the data collected: (1) the average mean diameter for particles on each stage came from microscopy (Appendix Tables 28-43); it was assumed that the mineral particles on stages 6 and 7 averaged 0.28 μm and all auto emission particles were 0.08 μm ; (2) the average particle volume was estimated by simply cubing the average diameter; (3) the density of minerals (and flyash) was assumed to be 2.7 and auto emission at 2.3 (2.7 is the average density of clay and 2.3 that of carbon black); (4) the percentage composition, by volume, was previously estimated (Appendix Table 51); and (5) the mass loading information provided by EPA (Table 2).

Table 2

Mass Loading of Trout Farm 8-Stage Anderson Impactor,
16 November 1973

Stage	Δ mass		Concentration ($\mu\text{gm}/\text{m}^3$)
	(μgm)	(%)	
0	325	(16.1)	8.4
1	216	(10.7)	5.6
2	234	(11.6)	6.0
3	366	(18.2)	9.4
4	236	(11.7)	6.1
5	111	(5.5)	2.9
6	53	(2.6)	1.4
7	65	(3.2)	1.7
Backup	410	(20.3)	10.6
Total	2016	(100.0)	51.9

Using the relationship

$$n = \frac{w}{\bar{V}_p d} (\text{pc})$$

where "w" is the mass loading of an impactor stage in grams, " $\bar{V}_p$ " is average particle volume in mm^3 , "d" is the density in grams/mm^3 and "pc" is the volume percentage composition of mineral and auto emission calculated to be on any one stage. Then "n" becomes the number of particles of a selected category on a specific stage. For all stages, there were approximately 6.00×10^7 particles averaging $> 1.0 \mu\text{m}$ in diameter and 2.29×10^{10} particles $< 1.0 \mu\text{m}$; this gives an atmospheric concentration for the sampling period of 16 November at the Trout Farm sampling location of 1.55×10^6 particles/ m^3 $> 1.0 \mu\text{m}$ and 5.89×10^9 particles/ m^3 $< 1.0 \mu\text{m}$.

IV. EDS Survey of Anderson 8-stage Impactor Stages 3-7 for Various Locations and Dates

EDS X-ray data for the Trout Farm Anderson impactor using Millipore substrates for 14, 16, 17 and 21 November are presented in Appendix Tables 47a, 48a, 49a and 50a; similar data for Adams County Fairground using Nuclepore substrates for 14, 16 and 21 November are presented in Appendix Tables 47b, 48b, and 50b. Figure 8 presents the relative percent intensities of silicon, potassium, sulfur/lead and lead emission lines.

DISCUSSION

I. Anderson Evaluation

From the information derived from the 16 November Anderson 8-stage impactor it is clear that there is little or no significant difference in particle size distribution across the surface of the Millipore substrates or backup filter; X-ray analyses suggest the same conclusion. It is also apparent that while the impactor does separate particles by size, large variation exists on each stage. It is also apparent that the average size of flyash and mineral particles on the same stage is significantly different. This might occur because the flyash is hollow; X-ray analysis and limited transmission electron microscopy suggest that the flyash particles are solid, from which we conclude that the differential separation of flyash and mineral particles is probably due to morphology or agglomeration.

X-ray analyses and particle inventories show a significant separation of particle types by composition: mineral particles (or particles with a chemical composition similar to minerals) were a major component by mass on all stages, overwhelmingly so on stages 0-3; flyash were obvious on all stages but mostly on stages 3-5; lead-containing compounds were most concentrated on stage 5 and sulfur was concentrated in stages 6 and 7.

II. Particulate Composition of the Urban Plume at the Trout Farm, 16 November 1973

By volume and mass, the major species of particles examined are minerals $> 1.0 \mu\text{m}$ in diameter, of which the most prevalent are clay, potassium aluminum silicates and quartz in relative abundance. Minerals also make up the major portion of the fluorescing material of particles $< 1.0 \mu\text{m}$. Lead, sulfur and zinc were most abundant in the last three Anderson stages: lead was observed in particles of lead (oxide), lead bromochloride, flyash and diffusely in auto emission; zinc was found as particles of zinc chloride, associated with lead and in flyash; sulfur was not observed in distinct particles though it was found associated

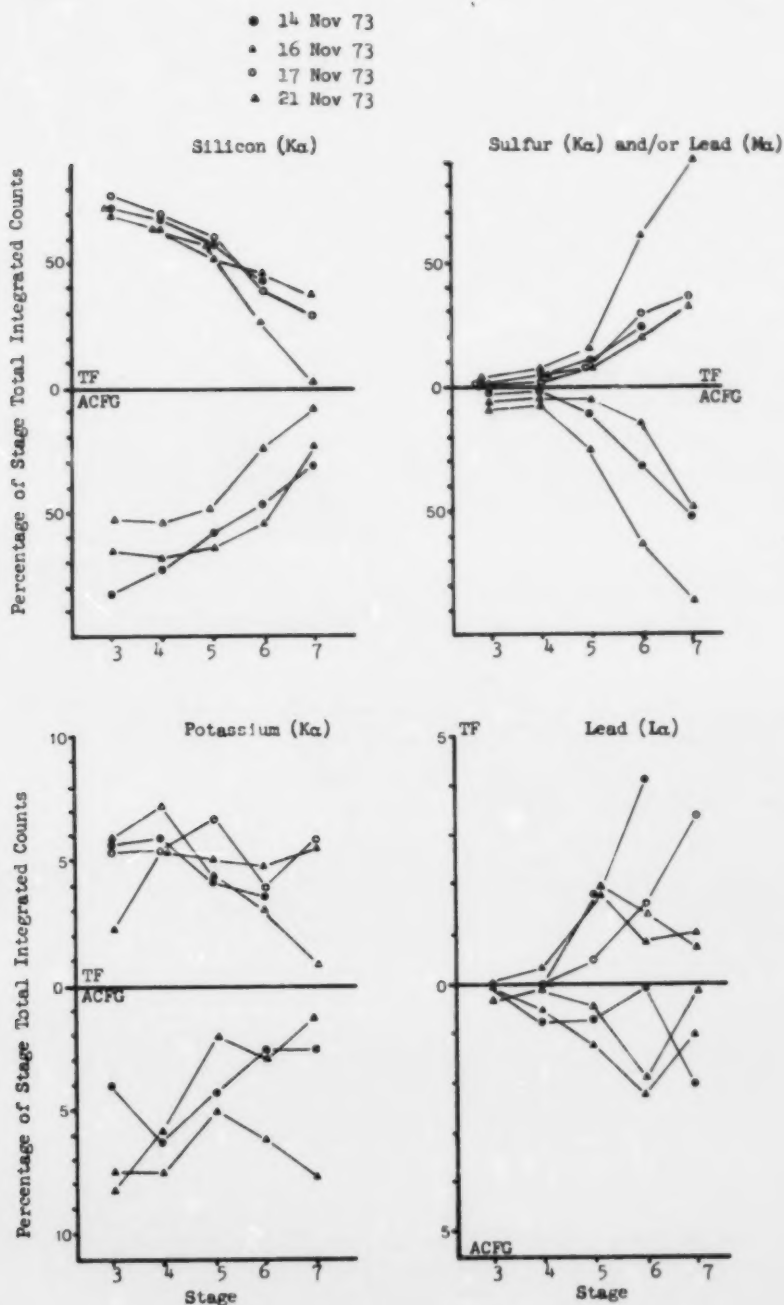


Fig. 8. Relative stage intensities for silicon $K\alpha$, potassium $K\alpha$, lead $M\alpha$ and/or sulfur $K\alpha$, and lead $L\alpha$ X-ray emissions for the Trout Farm sampling site 14, 16, 17 and 21 Nov. 1973 and Adams County Fairground sampling site 14, 16 and 21 Nov. 1973.

with some flyash and zinc particles, and was diffusely associated with auto emission. Sulfur predominance in the last impact stage suggests that it is associated with the smallest particles discriminated by the Anderson impactor.

III. Particle Size Distribution

Although it was estimated that the number of particles $< 1.0 \mu\text{m}$ was approximately 3 orders of magnitude greater than particles $> 1.0 \mu\text{m}$, the majority of smaller particles were auto emission particles which were observed in agglomerations on the various stages. Because of the nature of the Anderson impactor it is not possible to determine the size of these agglomerations on the various stages. Because of the nature of the Anderson impactor it is not possible to determine the size of these agglomerations prior to sampling and thus the Anderson sample will not allow determination of the atmospheric particulate frequency--particularly in an aged plume where agglomerates are more prevalent (Willeke 1974).

IV. EDS Survey of Anderson 8-Stage Impactor Stages for Various Dates, Locations and Substrate Materials

The results of the EDS survey suggest that both the Trout Farm and Adams County Fairground sampling locations experienced similar environments and fractioned particles into similar size groups. Lead and lead bromochloride particles were concentrated in stages 5 and 6 in similar amounts for the 14, 16, 17 and 21 sampling dates. Sulfur was always concentrated in stages 6 and 7 and increased significantly on 21 November. As the lead contribution remained relatively steady for all dates it would suggest that auto emission remained relatively constant while the sulfur component was introduced from another source.

CONCLUSIONS

1. While the majority of particles, by mass and volume, are relatively large minerals, the smaller particles are more numerous and are dominated by mineral (or particles with a chemical composition similar to predominant minerals in Denver's plume) and auto emission species
2. While the overall composition of the plume remained relatively stable for a 24 hour sampling period, non-mineral sulfur was observed to increase significantly during one sampling period (21 November) while the lead concentration remained at the same level during all sampling periods, suggesting a non-automotive source of sulfur.
3. The Anderson 8-stage impactor effectively separates most auto

emission particulates and associated sulfur onto the last two Anderson impact stages. However, the spots produced during impactation make direct observation and identification of particulates difficult, particularly on stages 6 and 7.

4. Morphological differences between flyash and mineral particles allow differential deposition of particles of flyash and minerals on the same stages. Flyash is not found in any significant amount on any stage where its presence would not be predominated by mineral particles.
5. Because of the chemical composition of flyash and its non-preferential impactation on any stage, X-ray fluorescence analysis for flyash is considered improbable.
6. The observation that many of the small particulates $< 1.0 \mu\text{m}$ are those produced by automotive and combustive sources indicates the need for fine particulate air standards to assess the cause of production. Present methods will not allow simultaneous size and chemical composition determination.

ACKNOWLEDGEMENTS

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ADDENDUM

Preliminary analyses of research funded under EPA contract 5-02-4108J indicate that flyash particles less than $1.0 \mu\text{m}$ may be significant contributors to material impacted on stages 5, 6 and 7 of the Anderson impactor. Examination of Millipore LoVol Filters exposed successively for short periods (2 hours) indicates that auto emission and flyash occurrence very dramatically increases during southerly air mass movement up the Platte River basin.

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APPENDIX TABLES

Appendix Table 1. Particles observed on the outer portion of stage 0 of the Andersen 6-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	5.4	Si, Al	K, Ca	--	clay	
2	6.2	Si	--	Mg	quartz	
3	1.4	Si, Al	K, Ca, Fe	Ti	flyash	conglomerate
4	2.8					
5	2.6					
6	1.9					
7	3.3					
8	2.5					
9	1.4					
10	2.8					
11	1.6					
12	1.3					
13	1.1					
14	1.4					
15	1.0					
16	0.7					
17	0.5					
18	0.3					
19	0.5					
20	1.8					
21	1.1					
22	0.3					
23	0.5					
24	8.1	Si	Al, Fe	K, Ca, S/Pb, Cl	clay	probably gypsum
25	5.6	Si	--	--	quartz	
26	3.2	Si	Al, K	--	aluminum silicate, potassium	
27	2.7	Si	Al, Fe	K, Ca, Ti	clay	
28	6.5	Si, Fe	K, Al	MgCl	aluminum silicate, iron	
29	7.0	Si	Al, K, Fe	Ti, Mg	aluminum silicate, potassium	
30	12.5	Si, Al	K, Fe	--	aluminum silicate, potassium	
31	4.0	Si	Al	K, Ca, Fe, Mg	flyash (Si rich)	
32	7.0	S, Ca	Si, Cl	Mg, Al, K	--	
33	1.8	Si	Al, K, Ca, Fe	--	clay	
34	3.9	--	--	Al, Si, Cl	auto emission	
35	3.8	Si, Al	Ca	K	aluminum silicate, calcium	
36	17.0	Si, Al	--	S/Pb, K, Ca, Fe	aluminum silicate, clay	
37	4.1	Si	Al	--	aluminum silicate, clay	
38	4.3	Si	--	Fe	quartz	
39	4.9	Si	--	K, Ca, Fe	quartz	
40	5.4	Si	Fe, Al	K, Ca	aluminum silicate, iron	
41	7.3	Si	Al, Fe, Ca	K, Ti	clay	
42	9.2	Si	K, Al	--	aluminum silicate, potassium	
43	6.5	Si	Al, K, Ca, Fe	Ti, S/Pb, Cl	clay	
44	3.9	--	--	--	auto emission	

Appendix Table 2. Particles observed on the middle portion of stage 0 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	4.4	Si, Al	K, Ca, Fe	--	flyash (Si rich)	
2	10.1	Si	Al, Ca	Pb/S, Cl, K, Fe	aluminum silicate, calcium	
3	7.6	Si	Al, Ca	--	aluminum silicate, calcium	
4	10.2	Si	--	--	quartz	
5	2.9	Si	Al, K	Fe	aluminum silicate, potassium	
6	2.3	Si	Al	K, Fe	clay	
7	2.2	Si	Al	Fe	clay	
8	1.7	Si	Al	K, Ca, Fe	clay	
9	6.6	Si, Al	K, Fe	Mg	aluminum silicate, potassium	
10	9.4	Ca	Si	--	mineral	
11	5.5	--	Ca, Si	Al, Mg, Fe, Pb/S	aluminum silicate, calcium	probably calcite conglomerate
12	1.2	Si, Al	--	Ca, Ti, Fe	flyash (Si rich)	
13	1.0	Si, Al	--	K, Ca, Fe	flyash (Si rich)	
14	2.4	Si, Al	Ca	Fe	aluminum silicate, calcium	
15	1.7	Si, Al, Ca	Ti, Fe	--	flyash (Ca rich)	
16	2.5	Si, Al	Fe	K, Ca, Ti, S	flyash (Si rich)	
17	1.7	Si, Al	--	Ca, Fe, Ti, K, Pb/S	flyash (Si rich)	
18	1.7	Si, Al	Ca, Fe	K, Ti	aluminum silicate, calcium	
19	1.7	Si, Al	Ca, Fe	Ti	flyash (Ca rich)	
20	1.4	Ca	Si, P	Fe, Al	flyash (Ca rich)	
21	5.0	--	--	--	auto emission	
22	3.0	Si, Al	Fe	K, Ca	clay	
23	10.9	Si	Al, K	--	aluminum silicate, potassium	
24	1.4	Si	Al	K	aluminum silicate, potassium	associated w/#23
25	1.4	Si	Al, K	--	aluminum silicate,	associated w/#23
26	4.8	Si, Al	--	K, Fe	clay	
27	3.6	Si	Al	K, Ca, Fe	clay	
28	3.7	Si	Al	--	clay	
29	14.7	Si, Al	--	K, Ca, Fe	clay	
30	6.0	Si, Al	--	Fe, K, Ca, Cu	flyash (Si rich)	
31	7.0	Si	--	Al	quartz	
32	8.2	Si	Al	K, Mg, Fe, Co	clay	
33	11.4	Si	Al	K, Ca, Fe	clay	
34	5.1	Si	--	Al, Ca, Fe	quartz	

Appendix Table 3. Particles observed on the center portion of stage 0 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	7.7	Si	Al,K,Ca,Fe	--	clay	
2	10.7	Si	Al	K,Ca,Fe	clay	
3	5.9	Si,Al,K	--	Fe	aluminum silicate, potassium	
4	8.8	Si	Al,K	Fe	aluminum silicate, potassium	
5	6.7	Si,Al	K	Fe	aluminum silicate, potassium	
6	7.1	Si	Al,Ca,K,Fe	--	flyash (Si rich)	
7	11.1	Si	--	Al	quartz	
8	6.2	Si	Al	K,Ca,Fe,Mg	clay	
9	9.6	Si,Al	K,Fe	Ca	clay	
10	3.4	Si	Al,K,Ca,Fe	Pb/S,Ti	flyash (Si rich)	
11	7.8	Si	--	Al,Mg,K,Fe	quartz	
12	10.5	Si	Al,S,K,Ca,Fe	Cl,Ti,Mg	clay	
13	6.2	Si,Al	K	Fe	aluminum silicate, potassium	
14	4.5	Si,Al,Ca,S	Fe,Ti	Mg,P,V,K	flyash (Ca rich)	
15	6.2	Si	Al,Ca,K	Mg,Fe	clay	
16	7.5	Si	Al,K,Ca	Fe	clay	
17	9.5	Si	Al,K,Fe	Ca,Ti	clay	
18	7.3	Si,K	Al	--	aluminum silicate, potassium	
19	5.7	Si	Al	--	clay	
20	4.0	Ca	Si	Al,Mg,K,Fe	mineral (Ca)	probably calcite
21	9.8	Si,S,Ca	Al	Mg,P,K,Fe,Zn	mineral (Ca/S)	
22	2.0	Si	Al,K,Ca,Fe	S,Ti	flyash (Si rich)	
23	0.6	Si	Al,Ca,Fe	K,S	flyash (Si rich)	
24	2.5	Si	Al,K,Ca,Fe	Pb/S	clay	
25	8.7	Si	--	--	quartz	
26	6.0	Si	Al,K,Ca,Fe	Mg	clay	
27	5.0	Si	--	Al,K,Fe	quartz	
28	3.4	Ca,Al,Si,P	Ti,Fe	--	flyash (Ca rich)	conglomerate
29	1.1	Ca,Al,Si	P,Fe	S,Ti	flyash (Ca rich)	
30	2.2	Si	Al,Ca	S,K,Fe	clay	
31	2.1	Ca,Si	Al,P,Fe	Mg,S,Ti	flyash (Ca rich)	
32	1.5	Si,Ca,Al	Fe	Ti,S	flyash (Ca rich)	
33	2.6	Si,Al,Ca	Fe,Ti	Mg	flyash (Ca rich)	
34	2.2	Si	--	Mg,Al,Ca,Fe	quartz	
35	5.4	Fe	--	Si,P	iron oxide	convoluted surface
36	3.6	Al,Ca	Fe	Mg,Si,Ti	flyash (Ca rich)	
37	2.4	Fe	--	Si	iron oxide	
38	13.2	Si	Al	K,Ca,Fe	clay	
39	5.5	Si	--	Al,K,Fe	quartz	
40	6.8	Si	Al,K,Fe	Mg,Ti	aluminum silicate, potassium	

Appendix Table 4. Particles observed on the outer portion of stage 1 of the Andersen 6-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	14.2	Si	Al,K,Ca,Fe	--	clay	
2	5.0	Al, Si, Fe, Ca	S	P, Ti	aluminum silicate, calcium and iron	
3	8.0	Si	Al,K,Ca,Fe	Ti, Pb/S, Cl	clay	
4	2.5	--	--	Al, Si	organic	
5	6.8	Si	--	--	quartz	
6	7.0	--	--	Al, Si, Pb/S, Cl	organic	
7	2.3	--	--	Mg, Al, Si, S/Pb	auto emission	
8	5.3	Si	Al	K, Ca	clay	
9	4.4	Si	Al, Ca	Fe, K, Cl, S	aluminum silicate, calcium	
10	3.9	Si, Ca	Al	K, Fe, Mg, Cl	aluminum silicate, calcium	
11	2.6	Si	Al, K, Cu, Fe	--	clay	
12	3.0	Ca, Si	--	Al, Fe	calcium mineral	probably calcite
13	1.6	Si	Al, K, Ca, Fe	S	clay	
14	1.8	Ca, Si	Al, K	Mg	calcium mineral	probably calcite
15	4.3	Si	--	Ca	quartz	
16	0.8	Si	Al	S, K, Ca, Fe	clay	
17	1.0	Si	Al, Fe	Mg, S, K, Ca	clay	
18	8.0	Si	Al, K	Ca, S, Fe	aluminum silicate, potassium	
19	16.0	Si, Al	K	Fe	aluminum silicate, potassium	
20	12.5	Si	Al, K, Ca, Fe	--	clay	
21	8.5	Si	Al, K	Fe, Cu	clay	
22	6.0	Si	Al, K, Ca, Fe	--	clay	
23	7.5	Si	Al, K, Ca, Fe, S	Cl	clay	
24	5.5	Ca	Si	Al, Fe	calcium mineral	probably calcite
25	3.0	Si	--	Al, K, Ca, Fe, Mg	quartz	
26	11.5	Si	Al, S, K, Ca, Fe	--	clay	
27	4.8	Si	Al, Fe	Cl, K, Ca, Ti	clay	
28	7.3	Si	--	--	quartz	
29	3.7	Si	Al, K, Ca, Fe	--	clay	
30	5.1	Si, Ca	Al, K, Fe	--	aluminum silicate,	
31	2.8	Si	--	Al, K, Ca, Fe	clay	
32	4.5	Si	Al, Fe	K, Ca	clay	
33	7.0	Si	Al	K, Ca, Fe	clay	
34	5.5	Si	Al, K	Fe	aluminum silicate, potassium	
35	1.7	Si	Al, K	Fe	aluminum silicate, potassium	
36	7.9	--	Si, Al	P, S, Cl, K, Ca, Fe	clay	
37	1.3	--	--	Si, Ca, Al, Si, S, Fe	organic	
38	2.7	--	--	Si, Al, Cu, S, Mg	organic	

Appendix Table 5. Particles observed on the middle portion of stage 1 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	7.7	Si	Al, Fe	K, Ca	clay	
2	8.3	Si	--	Al, K, Fe	quartz	
3	5.7	Si	Al, K, Ca, Fe	--	clay	
4	5.6	Ca	--	Al, Fe, Si	calcium mineral	probably calcite
5	4.2	--	--	Al, P, Cl, Ca	organic	
6	7.0	Si	Al, K	Pb/S, Ca, Fe	clay	
7	2.8	Si	Al	K, Ca	clay	
8	2.5	Si	Al, K	Ca, Fe	clay	
9	2.3	Si	Al	K, Ca, Fe	clay	
10	2.4	Si	Al, K	Fe	aluminum silicate, potassium	
11	3.1	Si	Al	K, Ca, Fe	clay	
12	3.1	Si	Al, K, Fe	Ca	clay	
13	12.8	Si	Al, S, K, Ca, Fe	P, Pb/S, Cl, Ti	clay	
14	4.2	Ca	Al, Si, S, Fe	P, Ti	flyash (Ca rich)	conglomerate ↓
15	1.7	Ca, Si	Al, Mg, Fe, S	P, Ti	flyash (Ca rich)	
16	1.2	Ca, Si	Al, S, Fe	--	flyash (Ca rich)	
17	3.6	Si, Al	Ca, Fe	Pb/S, K	flyash (Si rich)	
18	2.3	Ca, Fe	Si, Al, S	--	flyash (Ca rich)	
19	1.6	Si	Al, Ca, Fe	Pb/S, K, Cl	flyash (Si rich)	
20	1.7	Ca, Fe	Al, Si, S	K, Ti	flyash (Ca rich)	
21	2.2	Si, Ca	Al, S, Fe	P, K	flyash (Ca rich)	
22	4.1	S, Ca	--	Si	salt	
23	12.8	Si, Al	--	Cl, K, Fe	clay	
24	3.7	Si, Ca, Fe	Al	Pb/S, Cl, K	aluminum silicate, calcium and iron	
25	1.7	--	Ca, S	Al, Si	salt	
26	4.8	Si	Al, K, Ca, Fe	Pb/S	clay	
27	5.1	Si	Al, K	Cl, Ca, Fe	aluminum silicate, potassium	
28	6.8	Si, K	Al, Fe	P	aluminum silicate, potassium	
29	6.3	--	Si, Fe	Al, K, Ca	clay	
30	2.6	Si	--	Al	quartz	
31	4.5	Si	--	Al, K, Ca, Fe	clay	
32	3.3	Si	Al, K, Ca, Fe	Pb/S	clay	
33	5.4	Si	K, Al	Fe, Ti	aluminum silicate, potassium	
34	2.8	Si	--	K	quartz	
35	11.7	Si	Al, S, K, Ca, Fe	Pb/S	clay	
36	2.9	Si	Al	Mg	quartz	
37	3.4	Si	--	Al	quartz	
38	5.2	Si	Al, S, K, Ca, Fe	Ti	clay	
39	8.1	Si	--	Al, K, Ca, Fe	quartz	
40	5.6	Si	Al, K, Fe	Mg	aluminum silicate, potassium	
41	6.6	Si	K, Al	--	aluminum silicate, potassium	
42	9.7	Si	Al, K, Ca, Fe	--	clay	

Appendix Table 6. Particles observed on the center portion of stage 1 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	39.4	--	--	Pb/S	organic	
2	6.3	Si	Al, K, Fe	Ca, Ti	clay	
3	10.0	Si, Fe	Al	K, Ca, Mg	aluminum silicate, iron	
4	14.1	--	--	Al, Si, S, Ca, Fe	organic	
5	3.1	Si	Fe	K, Ca, Pb/S	clay	
6	12.9	Si	Mg	Fe	magnesium silicate	probably serpentine
7	4.1	Si	Al, K, Fe	Ti	aluminum silicate, potassium	
8	14.1	--	--	Si, Pb/S	organic	
9	5.5	Si	--	Fe	quartz	
10	2.2	Al, Si	--	Mg, Pb/S, Cl, K, Ca, Fe	clay	
11	3.1	Al, Si	K, Ca, Fe, S	Cl	clay	
12	4.5	Al, Si	K, Fe	Ca, Pb/S, Cl	aluminum silicate, potassium	
13	4.4	Al, Si	Fe	K, Ca	clay	
14	2.3	Al, Si	K, Fe	Ca, Pb/S	aluminum silicate, potassium	
15	2.9	Si	Al, K, Ca, Fe	--	clay	
16	2.7	--	--	Si, Pb/S	organic	
17	12.7	--	--	Si, Pb/S	organic	
18	9.4	Al, Si	K, Ca, Fe	Pb/S	clay	
19	7.8	Si	--	Fe	quartz	
20	10.0	Al, Si	Fe	K, Ca, Pb/S, Cl	aluminum silicate, iron	
21	9.7	Al, Si	Fe, K, Ca	Cl	clay	
22	3.1	Al, Si, S, Ca	Fe	K, Ti	mineral	possibly gypsum associated with an aluminum silicate
23	1.4	Al, Si	K, Ca, Fe	Cl, Mg	clay	
24	2.7	Al, Si, Fe	--	K, Ca, Ti, Mg	aluminum silicate, iron	
25	1.3	--	Al, Si, Fe	--	clay	
26	1.8	--	--	Si	carbon	angular shape
27	1.7	Al, Si	K	--	aluminum silicate, potassium	
28	2.7	Si	Al, K, Ca, Fe	Pb/S	clay	
29	3.3	Si	Al	Fe	clay	
30	4.6	Al, Si	K, Ca, Fe	S, Cl	clay	
31	2.9	Si	--	--	quartz	
32	3.4	Al, Si, Ca	--	--	aluminum silicate, calcium	
33	0.6	Al, Si	--	K, Ca, Fe	flyash (Si rich)	
34	1.6	Al, Si	Ca, Fe	--	flyash (Si rich)	
35	9.6	Al, Si	Fe	K, Ca, Pb/S	clay	
36	3.6	Al, Si	--	K, Ca, Fe, Pb/S	clay	
37	3.9	Si, Al, Ca	Fe	K, Pb/S, Mg	aluminum silicate, calcium	
38	6.4	Al, Si	Fe	K, Ca, Mg	clay	
39	5.7	Si, Fe	Al, K	Ti, Pb/S, Mg	aluminum silicate, iron	
40	7.9	Si	Al, K, Ca, Fe	Ti, Pb/S	clay	
41	2.2	Si	Al, K	Fe	aluminum silicate, potassium	
42	5.5	Si	Al, K	--	aluminum silicate, potassium	
43	3.3	Si	Al, K	--	aluminum silicate, potassium	
44	2.7	Si	Al	Mg, Pb/S, Fe	clay	
45	0.9	--	Si, Al	K	clay	
46	7.2	Si	Al, Fe	Ca	clay	
47	3.4	Si	--	Al, K, Fe	quartz	
48	2.1	Si	Al, Fe	K, Ca	clay	
49	6.4	Si	Al, K	--	aluminum silicate, potassium	
50	1.6	Si	Al	P, Pb/S, K, Ca, Fe, Cl	clay	
51	9.1	Si	Al, K, Fe	Ca	clay	
52	7.5	Si	Al, K, Ca	Fe	clay	
53	3.0	--	--	--	organic	
54	7.6	Si	Al, K, Fe	--	aluminum silicate, potassium	
55	7.8	Si	Al, K, Fe	Ca, Ti	clay	
56	12.3	Si	S, K, Ca, Fe	--	clay	
57	0.9	Si	Al, Fe, K	Ca, Cl	aluminum silicate, potassium	

Appendix Table 6. Particles observed on the center portion of stage 1 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973 (Con't)

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
58	[Deleted]					
59	6.3	Si	Al,K	Fe,Mg	aluminum silicate, potassium	
60	1.6	Si	Al,K	--	aluminum silicate, potassium	
61	3.9	Si	--	Al,Fe	quartz	
62	0.7	Si	Al	Mg,Fe	clay	
63	2.6	Si	Al,Fe	K,Cu	clay	
64	2.3	Si	Al	Fe	clay	
65	3.2	Si	Al,Fe	K,Ca	clay	
66	0.8	Si	Al	K,Cu,Fe,Cl	clay	
67	7.5	Si	Al,K,Fe	Ca	aluminum silicate, potassium	
68	4.6	Si	Al,Fe	K,Ca	clay	
69	4.1	Si	Al,K,Fe	--	aluminum silicate, potassium	

Appendix Table 7. Particles observed on the outer portion of stage 2 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	3.3	Si,Al	--	K,Ca,Fe	flyash (Si rich)	
2	1.8	Si,Al	--	S,K,Cu,Ti	flyash (Si rich)	
3	14.0	Si	Al,Cl,K,Ca, Fe	S,Ti,P,Mg	clay	
4	4.5	Ca,Si	Al	Fe,Mg,P,Fe	flyash (Ca rich)	
5	6.3	Si	Al,S,Ca,Fe	K,Cl	clay	
6	6.5	Si	Al,S,K,Ca,Fe	Mg,S/Pb,Cl,	clay	
7	5.1	Si,Al	--	K,Ca,Fe	clay	
8	5.5	Si	Al,K,Ca,Fe		clay	
9	3.8	Si	K,Al	Ca	aluminum silicate, potassium	
10	5.4	Si	--	--	quartz	
11	8.8	Si	K,Al	--	aluminum silicate, potassium	
12	7.5	Si	Al	S/Pb,K,Ca,Fe	clay	
13	5.5	Si	Al	Ca	clay	
14	1.8	Ca	Si	Al	calcium mineral	possibly asbestos or weathered calcite
15	12.0	Si	Al,K,Ca,Fe	Pb/S,Cl	clay	
16	6.0	Ca,Si	Al,K	Fe	aluminum silicate, calcium	
17	5.5	Si,Al	Fe	K,Ca	clay	
18	4.0	Si	K,Al	Fe	aluminum silicate, potassium	
19	9.0	Si	Al,K,Ca,Fe	Pb/S,Cl,Mg	clay	
20	4.6	Si	K,Al	Fe	aluminum silicate, potassium	
21	6.7	Si	Al,K,Ca,Fe	--	clay	
22	5.5	Si	--	Al,K,Ca,Fe	quartz	
23	2.6	Ca	Al,P,Si,Fe	Mg,S/Pb	flyash (Ca rich)	
24	5.0	Si	--	Mg,Al	quartz	
25	6.8	Si	--	Mg,Al,K,Ca,	quartz	
26	3.6	Si	K,Al	Fe Fe	aluminum silicate, potassium	
27	8.0	Si	Al,Fe	S/Pb,Cl,K,Ca	clay	
28	3.9	Si	K,Al	Fe	aluminum silicate, potassium	
29	2.2	Si	--	--	quartz	
30	4.7	Si	K,Al	--	aluminum silicate,	
31	3.4	Ti	--	--	TiO ₂	probably rutile
32	2.7	Si	Al,K	Fe	aluminum silicate, potassium	
33	3.8	Si	Al,K	Fe	aluminum silicate, potassium	

Appendix Table 8 Particles observed on the middle portion of stage 2 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	6.5	Si, Fe, K	Al, Ti	Mg	clay	conglomerate
2	8.4	Ca	Al, Si	S/Pb, Mg, Fe, Ti	flyash (Ca rich)	
3	2.6	Ca	Al, Si	S/Pb, Mg, Fe, Ti	flyash (Ca rich)	
4	1.6	Ca	Al, Si	S/Pb, Mg, Fe, Ti	flyash (Ca rich)	
5	1.2	Ca	Al, Si	S/Pb, Mg, Fe, Ti	flyash (Ca rich)	
6	0.4	Ca	Al, Si	S/Pb, Mg, Fe, Ti	flyash (Ca rich)	
7	1.8	Ca	Al, Si	S/Pb, Mg, Fe, Ti	flyash (Ca rich)	
8	1.8	Ca	Al, Si	S/Pb, Mg, Fe, Ti	flyash (Ca rich)	
9	1.7	Ca	Al, Si	S/Pb, Mg, Fe, Ti	flyash (Ca rich)	
10	1.7	Ca	Al, Si	S/Pb, Mg, Fe, Ti	flyash (Ca rich)	
11	2.1	Si, Ca	Fe	Al, Mg	flyash (Ca rich)	probably calcite
12	1.7	Si	Al, Ca, Fe	K	flyash (Si rich)	
13	2.2	Ca, Ti	Si, Fe	Mg, Al, P, S/Pb	flyash (Ca rich)	
14	5.3	Si	Al, Fe, K	Mg, P, Cl, Ca	clay	
15	14.0	--	K	Mg, Al, Si, F, Pb/S, Cl, Fe	carbon	
16	5.6	Ca	--	Si, P, Cl	calcium mineral	
17	2.5	Ca, Al, Si	Fe	Mg, P, Pb/S, Ti	flyash (Ca rich)	
18	1.4	Ca, Al, Si	Fe	Mg, P, Pb/S, Ti	flyash (Ca rich)	
19	5.1	Si	K, Al, Ca	--	aluminum silicate	
20	1.2	Si	Al, K, Ca, Fe	Ti, Mg, Pb/S, Cl	clay	morphology suggests asbestos
21	5.4	Si	Ca	K, Al	aluminum silicate, calcium	
22	5.2	--	--	--	carbon	
23	3.0	Si	--	Fe, Al, K	quartz	
24	4.0	Si, Fe, Al	Mg	K, Ca	aluminum silicate, iron	
25	5.5	Si	--	Al, K, Ca, Fe	quartz	
26	5.3	Ca	--	Al, Si	calcium mineral	
27	5.0	Ca	--	Al, Si	calcium mineral	
28	4.1	Si	Al, Ca, Fe	K	flyash (Si rich)	
29	3.9	Si, Al	S	K, Ca, Fe, Cl	clay	
30	1.3	Si	Al	Mg, Ca, Fe	clay	probably calcite
31	3.7	Si	--	K, Ca, Fe, Al	quartz	
32	7.2	Si, Al	K, Ca, Fe	--	clay	
33	6.0	Si	Al, K, Ca, Fe	--	clay	
34	3.0	Si	Al	--	clay	
35	4.0	Si	Al, Ca, Fe, K	--	flyash (Si rich)	
36	2.0	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
37	5.0	Si	--	--	quartz	
38	4.1	Si	Al, K, Ca, Fe	--	clay	
39	4.3	Si, Al	K	--	aluminum silicate, potassium	

Appendix Table 9. Particles observed on the center portion of stage 2 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (µm)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	7.9	Si	Al	K, Ca, Fe	clay	
2	4.9	Si	Al, Ca	--	aluminum silicate, calcium	
3	8.9	Si	Al, K, Ca, Fe	--	clay	
4	3.4	--	--	--	carbon	
5	7.5	Ca, Si	Al, K	Fe, Mg, Ti, P, Pb/S	aluminum silicate, calcium	
6	4.6	Si, Al	K	Fe	aluminum silicate, potassium	
7	5.0	Si	Al, Fe	K, Ca	clay	
8	3.3	Si	Al, Ca	--	aluminum silicate, calcium	
9	10.5	Si, Ca	Fe, Al, P	Cl, K	aluminum silicate, calcium	
10	5.3	Si	--	Al, K, Ca, Fe	quartz	
11	2.2	Si, Al	Fe, Ca, K	Mg, Ti, Pb/S	flyash (Si rich)	conglomerate
12	1.8	Si, Al	Ca, Fe	Mg, K, Ti	flyash (Ca rich)	
13	1.9	Si, Al	Ca, Fe	Mg, K, Ti	flyash (Ca rich)	
14	2.2	Ca	Al, Si, Fe	Mg, P, Pb/S, Ti	flyash (Ca rich)	
15	2.4	Si, Al	Fe, Ca, K	Mg, Ti, Pb/S	flyash (Si rich)	
16	1.6	Fe	--	Al, Si, Ca	flyash (Fe rich)	
17	0.6	Ca	Al, Si, Fe	Mg, P, Pb/S, Ti	flyash (Ca rich)	
18	2.2	Ca	Al, Si, Fe	Mg, P, Pb/S, Ti	flyash (Ca rich)	
19	1.0	Si, Al	Fe, Ca, K	Mg, Ti, Pb/S	flyash (Si rich)	
20	1.8	Si, Al	Ca, Fe	Mg, K, Ti	flyash (Ca rich)	
21	2.2	Ca	Al, Si, Fe	K, P	flyash (Ca rich)	
22	2.0	Si, Al	Fe, Ca, K	Mg, Ti, Pb/S	flyash (Si rich)	
23	2.9	Si, Al	Fe, Ca, K	Mg, Ti, Pb/S	flyash (Si rich)	
24	1.6	Si, Al	Ca, K, Fe	Pb/S	flyash (Si rich)	
25	2.2	Si, Al	Ca, K, Fe	Pb/S	flyash (Si rich)	
26	1.4	Si, Al	Ca, Fe	Mg, K, Ti	flyash (Ca rich)	
27	1.2	Si, Al	Ca, Fe	Mg, K, Ti	flyash (Ca rich)	
28	1.8	Ca	Al, Si, Fe	Mg, P, Pb/S, Ti	flyash (Ca rich)	
29	1.2	Si	Ca, Al, Fe	K, Pb/S	flyash (Si rich)	
30	0.7	Si	Ca, Fe, S	K, P	flyash (Si rich)	
31	1.2	Si	Ca, Al, Fe	K, Pb/S	flyash (Si rich)	
32	1.8	Si, Al	Ca, Fe, S	K, Ti	flyash (Si rich)	
33	1.7	Si, Al	Ca, Fe, Ti	Pb/S, Cl, K	flyash (Si rich)	
34	2.4	Si, Ca, Ti, Al	Fe	K, Ti	flyash (Ca rich)	conglomerate
35	1.0	Si, Ca, Ti, Al	Fe	K, Ti	flyash (Ca rich)	
36	1.8	Fe	--	Al, Si, Ca	flyash (Fe rich)	
37	5.5	Si	--	--	quartz	
38	10.5	Si	K, Al	--	aluminum silicate, potassium	
39	6.0	Si, Ca, Al	Fe	Pb/S, Ti, Mg	flyash (Ca rich)	
40	2.5	Si, Al	Ca, Fe	K, Ti	flyash (Si rich)	
41	7.0	Si	Al, K, Ca, Fe	Mg	clay	
42	3.3	--	--	K, Al, Cl, Pb/S, Si, P	carbon	
43	4.5	--	--	K, Al, Cl, Pb/S, Si, P	carbon	
44	6.5	Si	K, Al, Fe	--	aluminum silicate, potassium	
45	5.0	Ca	Si, Fe	Al, Pb/S, Mg, P	mineral calcium	probably calcite
46	6.5	Si	K, Al, Fe	--	aluminum silicate, potassium	
47	5.0	Si	Al, Cu	--	aluminum silicate, calcium	
48	5.0	Si	Al, K	Ca	clay	
49	6.0	Si	Al, Fe	K, Ca, Mg	clay	
50	3.0	Si, Al	K	--	aluminum silicate, potassium	
51	5.0	Ca	Fe, Al, Si	Mg, P, Pb/S, Ti	flyash (Ca rich)	
52	5.7	Si	Al	Ca, Fe	clay	
53	6.3	Si	Al, K, Ca, Fe	--	clay	
54	8.5	Si	K, Al	Fe	aluminum silicate, potassium	
55	8.8	Si	Al, Fe	K, Ca	clay	
56	4.5	Si	--	Al, Pb/S, K	quartz	

Appendix Table 10. Particles observed on the outer portion of stage 3 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	1.8	Si, Al	K, Ca	Mg	clay	
2	0.6	Si	Al	--	clay	
3	0.8	Si	Al	--	clay	
4	2.4	Si	Al, K	--	aluminum silicate, potassium	
5	1.6	Si, Al, K	Fe	Mg	aluminum silicate, potassium	
6	0.4	Fe, Al, Si	--	--	aluminum silicate, iron	
7	0.8	Si	--	Fe, Mg	quartz	
8	1.4	Ca	Al, Si, P, Fe	Mg, K	flyash (Ca rich)	
9	0.3	Fe	--	--	iron	
10	1.1	Si, Al	Fe	--	aluminum silicate, iron	
11	0.6	Si	--	--	quartz	
12	1.8	Si	Al, K, Ca	Fe	clay	
13	0.9	Si, Al	--	--	clay	
14	0.8	Si	Al, Ca, S	Fe	aluminum silicate, calcium	
15	4.0	Si	Al, K	--	aluminum silicate, potassium	
16	0.9	Si	Al	K, Ca	clay	
17	2.0	Ca	Mg, Si	Fe	mineral calcium	probably dolomite
18	1.7	Si	--	--	quartz	
19	0.6	Si	Al, K	--	aluminum silicate, potassium	
20	2.4	Si	--	Al, Fe	quartz	
21	1.9	Si	Al, K	Mg, Fe	aluminum silicate, potassium	
22	0.6	Si	Al	--	clay	

Appendix Table 11. Particles observed on the middle portion of stage 3 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (µm)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	1.9	Ca	Mg	Si	mineral calcium	probably dolomite
2	2.9	Si	Al, K, Fe	Ca	clay	
3	2.7	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
4	3.0	Si	Al, K, Fe	Ca	clay	
6	2.9	Si	Al, K, Fe	Ca	clay	probably rutile
8	0.9	Si	Al, K	--	aluminum silicate, potassium	
9	2.3	Si	Al, Fe	--	aluminum silicate, iron	
10	2.9	Si	Al, K, Ca, Fe	--	clay	
11	1.0	Si, Ca, Fe	Al	--	flyash (Ca rich)	
12	1.0	Si	Al	K, Ca, Fe	flyash (Si rich)	
13	0.8	Ti	Si, Al, Fe	K, Ca	mineral titanium	
14	1.0	Pb, Cl	Br	--	lead bromochloride	
15	2.7	Si	--	--	quartz	
16	2.8	--	--	Al, Si, S, Cl, K, Ca	carbon	
17	1.5	Ca	Si, Al, Fe	--	mineral calcium	
18	3.3	Si	Al, K, Ca, Fe	--	clay	
19	1.9	Si, Al	--	Fe	clay	
20	2.0	--	--	--	carbon	
21	1.2	--	--	--	↓	
22	1.1	--	--	--		
23	0.7	--	--	--		
24	1.4	--	--	--		
25	0.6	--	--	--		
26	2.2	--	--	--		
27	1.0	--	--	--		
28	(filter)	--	--	--		
29	1.0	--	--	--		
30	1.6	--	--	--		
31	2.4	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
32	0.9	Si	--	Fe, Al	quartz	
33	0.5	Si	Al, K, Ca, Fe	--	clay	
34	1.5	Si	--	--	quartz	
35	1.7	Si	Al, K, Ca	--	clay	
36	1.1	Si	Al, K, Fe	--	aluminum silicate, potassium	
37	2.7	Ca	--	Si, Fe	mineral calcium	
38	0.8	--	--	--	carbon	
39	1.9	Si	Al, K, Ca, Fe	--	clay	
40	1.9	Si	Al, K, Ca, Fe	--	clay	
41	1.5	Si	Al, K, Ca, Fe	--	clay	
42	0.6	Si	Al, K, Ca, Fe	--	clay	
43	0.7	Si	Al, K, Ca	--	clay	
44	0.9	Si	Al, K, Ca, Fe	--	clay	
45	0.5	Si	Al, K, Ca, Fe	--	clay	
46	0.4	Si	Al, K	--	aluminum silicate, potassium	
47	0.50	Si	Al, K, Ca, Fe	--	clay	
48	0.5	Si	--	--	quartz	
49	2.6	Si	--	--	quartz	
50	0.9	Si	Al, K, Ca, Fe	--	clay	
51	1.7	Si	Fe	--	quartz	
52	2.5	Si	--	Fe	quartz	
53	1.5	Si	Al, K, Ca, Fe	--	clay	
54	1.8	Fe	Si, Ti	--	mineral iron	
55	1.1	Si	Al	--	clay	
56	2.4	Si	Al, K, Ca, Fe	--	clay	
57	5.8	--	Pb, S	Br, Cl	auto emission	
58	1.6	Si	Al, K, Ca, Fe	--	clay	
59	2.9	Si	Al, K, Fe	--	aluminum silicate, potassium	

Appendix Table 12- Particles observed on the center portion of stage 3 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	1.2	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
2	0.9	Ca	Al, Si, Fe	--	flyash (Ca rich)	
3	1.0	Si	Al, K, Ca, Fe	--	clay	
4	0.5	Si	Al, K, Ca, Fe, S	--	flyash (Si rich)	
5	1.2	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
6	2.3	Si	Al	--	clay	
7	2.2	Si	Al, K, Ca, Fe	--	clay	
8	4.0	Si	Al, K, Ca, Fe	--	clay	
9	2.8	Si	Al, K	--	aluminum silicate,	
10	2.6	Ca	P, Si	--	potassium	
11	2.3	Ca	P, Si, Fe	K, Al	mineral calcium	probably apatite
12	2.5	Fe	Si	Al, K, Ca	mineral iron	possibly fractured from #10
13	1.3	Si	Al, K, Ca, Fe	--	clay	possibly weathered quartz
14	2.3	Si	Al, K, Ca, Fe	--	clay	
15	4.3	Si	Al, K	--	flyash (Si rich)	
16	1.0	Si	Al, K, Ca, Fe	--	clay	
17	1.6	Si	Al, Ca, Fe	--	flyash (Si rich)	
18	2.5	Si	Al	K, Fe	clay	
19	3.4	Si	Al, K	--	aluminum silicate,	
20	3.0	Si	K, Al, Ca, Fe	--	potassium	
21	2.2	Al, Si	--	K, Ti, Fe	flyash (Si rich)	
22	1.6	Si	Ca	K, Fe, Al	clay	
23	0.7	Si	Al	Ca, Fe	clay	
24	3.0	Si	--	--	quartz	
25	4.1	Si	Al, K, Fe	--	aluminum silicate,	
26	1.7	Ca, Si	Al	K, Fe	potassium	
27	0.7	Si, Al	--	--	aluminum silicate,	
28	1.3	Si, Al	K, Fe, Ca	--	calcium	
29	1.8	Si, Al	--	--	clay	
30	2.0	Ca	Si	--	clay	
31	2.5	Si	--	--	mineral calcium	probably calcite
32	2.5	Si	Al, K, Ca, Fe	--	quartz	
33	1.5	Si	Al, K	--	clay	
34	2.1	Fe, Ca, Si	Mn	Zn	aluminum silicate,	
35	1.8	Si	Al, K, Ca, Fe	--	potassium	
36	2.0	Si	--	Al, Fe	mineral-Fe, Ca, Si	
37	2.5	Si	Al, K, Ca, Fe	--	clay	
38	2.4	Si	--	Al, Fe	quartz	
39	1.9	Ca	Al, Si, P, Fe	--	clay	
40	2.7	Si	Al, K, Ca, Fe	--	flyash (Ca rich)	
41	1.1	Si	Al, K, Ca, Fe	--	clay	
42	3.0	Si	Al, Ca, Fe	Ti	clay	
43	1.4	Ti	Fe	Al, P, Si	aluminum silicate,	
44	2.9	Si	Al, K, Ca, Fe	--	calcium	
45	2.2	Si	Al, K, Ca, Fe	--	mineral titanium	probably rutile
46	2.4	Al	Al, K, Ca, Fe	--	clay	
					aluminum (oxide)	

Appendix Table 13 Particles observed on the outer portion of stage 4 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	1.6	Al, Si, S	--	--	mineral	fluorescence similar to that of ultramarine
2	1.5	Si, Fe, Ca	Al	--	aluminum silicate,	
3	2.3	Si, Al	K, Fe	Ca	calcium and iron	
4	2.0	Si, Fe, Ca	Al	--	clay	
5	1.3	Si	Mg, Al, Pb, S,	--	aluminum silicate,	
6	1.0	Si, Al	Cl, K, Ca, Fe	--	calcium and iron	
7	1.1	Si	Fe	Ca, K, Pb/S	clay	
8	0.8	S, Cl	Al, K, Ca, Fe	--	aluminum silicate,	
9	0.5	Si, Al, S, Ca	--	Si, Al, Ca	calcium and iron	
10	1.6	Al, Si, Ca, Fe	Cl, Ti, Fe	Mg, K	unknown (salt)	
11	1.0	Si	--	--	flyash (Si rich)	
12	1.2	Si, Al	Al, K, Ca, Fe	--	flyash (Ca rich)	
13	1.2	Si	Fe	--	flyash (Ca rich)	
14	1.0	Si, Al	--	--	clay	
15	1.3	--	Ca, Fe	--	flyash (Si rich)	
16	1.4	--	Al, Si	--	quartz	
17	2.2	Si	Al, Si	--	flyash (Si rich)	
18	1.3	Si	Al, K	--	carbon	
19	1.5	Si	Al, K	--	aluminum silicate,	
20	1.8	Si	Al, K, Ca	--	potassium	
21	1.0	Si, Al	--	--	aluminum silicate,	
22	0.9	Fe	--	Al, Si	potassium	
23	1.8	Si	Al, K	--	clay	
24	0.6	Si	Al, K	--	flyash (Si rich)	
25	1.0	Ca, Ti	Al, Si, Fe	--	flyash (iron)	
26	1.1	Si, Al	K, Ca, Fe	--	aluminum silicate, potassium	
27	0.9	Si, Al	Ca, Fe	--	flyash (Ca rich)	
28	1.4	Si	Al, Mg, K, Ca, Fe	--	flyash (Ca rich)	
29	0.8	Si	--	--	clay	
30	0.8	Si, Fe	Al	--	quartz	
31	1.2	Si	Al, K, Ca, Fe	--	aluminum silicate, iron	
32	0.9	Si	K	Al	flyash (Si rich)	
33	1.2	Si	K, Fe	Al	aluminum silicate,	
34	1.0	Si	Al, K, Ca, Fe	--	potassium	
35	0.7	Pb	--	--	clay	
36	1.6	Ca, S	Si	--	Lead (oxide)	
37	0.6	Ca	Si, Al	--	mineral calcium	probably calcium sulfate
38	1.2	Si	Al, K, Ca, Fe, Pb, Cl	--	mineral calcium	probably calcite
39	1.4	Si, Fe	Mg, Al, K, Ca	--	clay (w/lead chloride)	
40	0.9	Si	--	--	aluminum silicate	probably asbestos
41	0.7	Si	Al, K, Ca, Fe	--	quartz	
42	1.1	Si	Al, K, Ca	--	clay	
43	0.6	Si	Al, Fe	K, Ca	clay	
44	0.7	Si	Al	K, Ca, Fe	clay	
45	1.2	Pb	Cl, Br/Al	--	lead bromochloride	
46	0.6	Pb	Cl, Br/Al	--	lead bromochloride	
47	1.8	Si	Al, K, Ca, Fe	Pb/S	clay	
48	0.9	Fe	Mg, Si, Cr, Mn, Zn	--	iron	probably steel
49	1.1	Si, Al	Fe, Ca	K	flyash (Si rich)	
50	1.2	Ca	Al, Si	--	mineral calcium	probably calcite
51	1.4	--	--	Cl, K, Ca	carbon	
52	0.6	--	--	--	carbon	
53	1.1	Ca	--	--	mineral calcium	probably calcite
54	0.9	Fe	--	Al, Si, Ca	iron, mineral	
55	1.4	Si, Al	K, Ca, Fe	--	clay	
56	1.3	Si, Al	--	Mg, K, Ca, Fe	flyash (Si rich)	

Appendix Table 14. Particles observed on the middle portion of stage 4 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	1.3	Si, Al	K, Ca	Mg, Ti, Cr, Fe	flyash (Si rich)	
2	2.0	Si, Al	Ca, Fe	Mg, K, Ti	flyash (Si rich)	
3	0.8	Si, Al	--	Mg, Fe, K, Ca	flyash (Si rich)	
4	0.8	Ca, Al	Si, Fe, K	--	flyash (Ca rich)	associated
5	1.0	Si, Al	K, Ca, Fe	--	flyash (Si rich)	"
6	3.0	Si	Al, Fe	K, Ca	clay	
7	1.6	Si, Al	K, Ca	Fe	clay	
8	0.5	Ca	Al, Si, Fe, Mg	--	flyash (Ca rich)	associated
9	1.0	Si, Al	Ca, Fe	K, Mg	flyash (Si rich)	"
10	1.8	Si	--	Mg, Fe	quartz	
11	1.2	Si	Al, K, Ca, Fe	--	clay	
12	0.4	Si	Al, K, Ca, Fe	--	clay	
13	1.2	Si, K	Al	--	aluminum silicate, potassium	
14	0.8	--	Al, Si, Fe	--	clay	
15	1.0	Si	--	K, Ca, Al, Fe	clay	
16	0.8	Si	K, Ca, Al	--	clay	
17	0.6	Si, Ca	Al	--	aluminum silicate, calcium	
18	3.3	Si, Al	K, Ca, Fe	--	clay	
19	1.2	Ca	S	Al, Si	calcium-sulfur	probably gypsum
20	0.6	Si	S, Ca, Al	--	clay	
21	0.7	Si	Al, Ca	--	aluminum silicate, calcium	
22	1.1	Si	Al, K, Ca	--	clay	
23	1.0	Si	Al, K, Ca	--	clay	
24	0.6	Si, Al	K, Fe	--	flyash (Si rich)	
25	0.7	Si	Al, K	--	aluminum silicate, potassium	
26	2.0	Si	Al	Fe	clay	
27	1.8	Si	Al	Fe	clay	
28	2.8	Si	Al, K, Ca, Fe	--	clay	
29	1.3	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
30	1.3	Si, Al, Ca	Fe	Ti	flyash (Ca rich)	
31	0.6	Si, Al	--	Fe, Pb/S, Cl, K, Ca	flyash (Si rich)	
32	1.1	Si	Al, K, Ca, Fe	Ti, V	flyash (Si rich)	
33	1.2	Si	--	--	flyash (Si rich)	
34	0.8	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
35	3.4	Si	--	Al, Pb/S, K, Ca, Fe	clay	
36	0.8	Si	--	--	flyash (Si rich)	
37	0.5	--	S, Ca	Al, Si, Cl	calcium-sulfur	probably gypsum
38	1.8	Si, K	Al	--	aluminum silicate, potassium	
39	0.6	Si, Al	--	Fe	clay	

Appendix Table 15. Particles observed on the center portion of stage 4 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	3.3	Si	Al, Ca	--	Aluminum silicate, calcium	
2	1.6	Si	Al	Fe, K, Ca	clay	
3	1.0	Si	Al	Fe, K, Ca	clay	
4	0.8	Si	Al	Fe, K, Ca	clay	
5	0.6	Si	Al, K, Ca, Fe	--	clay	
6	1.2	Si	Al, Ca	--	aluminum silicate, calcium	
7	1.3	Si	Al, Fe, K, Ca	--	clay	
8	2.0	Si	Al, K, S, Cl, Fe	--	aluminum silicate, potassium	
9	0.9	Fe	Al, Si	--	iron, mineral	
10	0.8	Si	Al, K, Fe	--	iron, mineral	
11	1.8	--	--	Si, Al, Pb/S, Cl, K, Ca	carbon	
12	0.8	Fe	--	Si	iron	
13	0.2	Si	--	Al, K, Fe	quartz	
14	5.2	Si, Al	Fe, K, Ca	Mg, Pb/S	clay	
15	1.6	Si	Al	--	clay	
16	1.0	Si	Al, Ca, Fe	K	flyash (Si rich)	
17	1.4	Si, Al	--	K, Ca, Fe	clay	
18	1.4	Si	--	--	quartz	
19	0.8	Si	--	--	quartz	
20	0.9	Si, Al, Ca	Fe, Mg	--	aluminum silicate, calcium	
21	0.9	--	Pb, Si, Al, Ca	Fe	aluminum silicate, calcium-with lead	
22	1.2	Al, Ca	Fe, Ti	--	flyash (Ca rich)	
23	2.2	Fe	--	Al, Si	iron	
24	1.0	Al, Pb	Fe, Br	Cl	flyash (Pb rich)	
25	2.1	Ca	--	Si	mineral calcium	probably calcite
26	1.2	Si	Al, K, Fe	Pb/S, Cl	aluminum silicate, potassium	
27	2.7	Si	Al, K, Fe	Pb/S, Cl	aluminum silicate, potassium	
28	1.1	Si, Ca	--	Mg, Al, Fe	flyash (Ca rich)	
29	1.4	Si	Al, K	--	aluminum silicate, potassium	
30	1.0	Si	Al, K, Ca, Fe	--	clay	
31	1.7	--	Si, Ca, Fe, Al	Pb/S, Cl, K	clay	
32	0.5	Si	Al, K, Ca, Fe	--	clay	
33	0.9	Fe, Si	Al, Ca, K	--	aluminum silicate, iron	
34	1.0	Si, Al	Fe	K, Ca	clay	
35	0.9	Si, Al	--	Ca, Fe	flyash (Si rich)	
36	0.7	Ca	--	Al, Si, Pb/S, Fe	mineral calcium	probably calcite
37	1.2	Si, Al	--	--	clay	
38	0.7	Si	Al, K	Pb/S	aluminum silicate, potassium	
39	1.6	Si	Al, K, Fe	--	aluminum silicate, potassium	
40	1.1	Si	Al, K, Ca, Fe	--	clay	
41	1.8	Si	Mg, Al, K, Fe	--	magnesium aluminum silicate	probably asbestos

Appendix Table 16. Particles observed on the outer portion of stage 5 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	1.3	Pb, Br	--	--	lead bromochloride	
2	0.3	Pb, Br	--	--	lead bromochloride	
3	1.2	Pb, Br	Al, Si, Zn	--	lead bromochloride	
4	0.4	Pb, Br	Si	--	lead bromochloride	
5	0.4	Si	Al, Ca, Fe	Pb/S	aluminum silicate, calcium clay	
6	0.5	Si	Al	--	metal	
7	0.5	Fe, Zn	--	Al, Si, Pb/S, Cl, K, Ca	metal	
8	0.4	Fe	--	Zn, Pb/S, Cl, K, Ca	iron	
9	0.3	Pb, Br	--	Cl, Ca, Fe	lead bromochloride	
10	0.3	Si, Fe, Mn	--	Al, Pb, Zn	silicate(?)	
11	0.4	Si	Al	--	clay	
12	1.4	Si	Al	Pb/S, K, Ca, Fe	clay	
13	0.8	Si	Al, K, Ca, Fe	Ti, Cr, V, Mn	flyash (Si rich)	
14	1.0	Pb, Br	--	--	lead bromochloride	
15	0.9	Si	Al, K, Ca, Fe	--	clay	
16	0.7	--	--	Cr	auto emission	
17	0.3	Br, Pb	Cl	--	lead bromochloride	
18	0.7	Zn, Pb	--	Br/Al	metal	
19	0.5	Zn, Pb	--	Al, Si, C	metal	
20	0.5	Si	--	--	quartz	
21	0.6	Si	--	--	quartz	
22	0.7	Pb, Br	--	--	lead bromochloride	
23	0.5	Br, Pb, Si	K, Ca, Ti, Fe	--	clay	associated w/auto emission
24	0.6	Si	Al, K, Ca, Fe	--	clay	
25	0.6	Si	Br, Pb, Ca	--	aluminum silicate, calcium	associated w/auto emission
26	0.5	Si	Br, Pb, K	--	aluminum silicate, potassium	associated w/auto emission
27	0.4	Si, Pb, --	--	--	quartz	
28	0.9	Pb, Br	K, Ca, P, Mn, Zn, Ti	--	lead bromochloride	associated w/auto emission
29	1.1	Si	Al/Br, Pb, K, Ca, Fe	--	clay	associated w/auto emission
30	2.0	Si	Al, K, Ca, Fe, Mg	--	flyash (Si rich)	
31	3.8	Si	Al, K, Ca, Fe, Mg	--	flyash (Si rich)	
32	1.6	Si	--	--	quartz	
33	0.5	Si, Al	Cl, Ca, Fe	--	aluminum silicate, calcium	
34	0.9	Pb, Br	Si	--	lead bromochloride	
35	0.6	Ca	--	--	mineral calcium	probably calcite
36	1.0	--	Al, Si, Ca, S	--	clay	
37	0.8	Si, Al	--	--	clay	
38	0.4	Si	--	--	quartz	
39	0.5	--	Al	Si, S, Cl	metal	
40	0.4	Ca	Al, Si	Fe	aluminum silicate, calcium	
41	0.3	--	--	--	carbon	
42	1.2	Si, Al	--	Ca	clay	
43	0.7	Pb, Br	--	Cl	lead bromochloride	
44	1.2	Si	Al	K, Fe	clay	
45	0.4	Ca	Al, Si	Pb/S, Fe	mineral calcium	probably calcite
46	1.9	Pb, Br, Cl	--	Zn, Fe	mineral calcium	
47	0.6	Si	Al, Ca	P/S	aluminum silicate, calcium	
48	0.4	Pb, Br	--	Cl	aluminum silicate, calcium	
49	0.6	Si	--	Al	quartz	
50	0.2	Si	--	Al	quartz	
51	0.6	Si	Al, Ca	--	aluminum silicate, calcium	
52	0.3	Pb, Br	--	Cl	aluminum silicate, calcium	
53	0.4	--	--	Pb, Br, Cl	auto emission	
54	0.6	Si	--	--	quartz	
55	0.6	Ca	Fe, Al, Si, S	Mg, P, Ti, Zn	flyash (Ca rich)	
56	0.7	Ca	Al, Si	Fe, Cl, Zn	aluminum silicate, calcium	
57	0.5	Ca, S	--	Al, Si, Cl, K	calcium-sulfur	probably gypsum
58	0.3	Pb, Cl	Br	Zn	lead bromochloride	
59	0.4	Pb, Cl, Br	--	--	lead bromochloride	
60	0.4	Pb, Cl, Br	--	--	lead bromochloride	

Appendix Table 16 (Con't). Particles observed on the outer portion of stage 5 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (µm)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
61	0.7	Al, Si, Ca, Fe	--	P	flyash (Ca rich)	
62	0.6	Ca	--	--	mineral calcium	
63	0.3	Pb	--	Cl, Br	lead (oxide)	probably calcite
64	0.6	Si, Al, Ca, Fe	--	--	aluminum silicate, calcium	
65	0.4	Si	Al, K, Ca, Fe	--	clay	
66	0.6	Si, Al	--	--	clay	
67	0.4	Si, Al	--	--	clay	
68	0.5	Si, Al	--	Fe, Ca, K	clay	
69	0.4	Si, Al	--	Fe, Ca, K	clay	
70	2.5	Si	--	Al	quartz	
71	0.5	Si, Al	--	--	clay	
72	0.7	Cl	Ca	Pb/S, P, Al, Si	chloride	probably calcium chloride
73	0.9	Cl	Ca	Pb/S, P, Al, Si	chloride	probably calcium chloride
74	0.5	Pb, Br	Cl	--	lead bromochloride	
75	1.4	Si, Ca	Al, K, Fe	--	aluminum silicate, calcium	

Note: Particles 1-29 associated with an amorphous mass giving a trace of Pb, Br; particles from 48-63, 66-69 associated with a more tenuous amorphous mass.

Appendix Table 17. Particles observed on the middle portion of stage 5 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (µm)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	2.9	Si, Al	Fe, K, Ca, Pb	--	clay	
2	0.6	Si	--	--	quartz	
3	1.7	Al, Si, Fe	--	K, Ca	aluminum silicate, iron	
4	1.0	Al, Si, Fe	--	K, Ca	aluminum silicate, iron	
5	0.6	--	Si	--	quartz	
6	0.6	Al, Si, Fe	--	K, Ca	aluminum silicate, iron	
7	0.7	Ca	Al, Si	--	flyash (Ca rich)	
8	1.3	Pb, Cl	--	Br	lead bromochloride	
9	0.9	--	--	--	carbon	
10	0.6	--	--	Pb/S	auto emission	
11	1.2	Zn, Cl	--	--	zinc chloride	
12	0.6	Si	--	--	flyash (Si rich)	
13	0.7	Si	--	--	quartz	
14	0.9	Si	Al, S	K, Ca, Fe	clay	
15	0.4	--	--	--	carbon	
16	1.2	Si, Al	--	--	clay	
17	0.6	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
18	0.4	Pb	Br, Cl	--	lead bromochloride	
19	0.5	--	Si, Al, Ca	P, S	clay	
20	0.8	--	--	--	flyash (carbon)	could also be latex or polyvinyl acetate spheres
21	0.3	Pb	--	Si	lead (oxide)	
22	0.8	Si	Ca, Fe	--	flyash (Si rich)	
23	0.6	Si	--	--	flyash (Si rich)	
24	0.6	Si	K, Ca, Fe	Pb/S	flyash (Si rich)	
25	0.7	--	--	--	flyash (carbon)	see particle #20
26	0.3	Ca, Al, Si, K	--	--	flyash (Ca rich)	
27	0.7	Al, Si, Ca	--	--	flyash (Ca rich)	
28	2.0	Al	--	Pb/S	quartz	
29	0.5	--	--	--	carbon	
30	0.4	Pb, Br	--	--	lead bromochloride	
31	0.6	--	--	--	flyash (carbon)	see particle #20
32	0.4	Zn, Pb	Al, Si, Fe	--	metal	
33	0.5	Si	Al, Fe	--	flyash (Si rich)	
34	0.6	Ca	Al, Si, Fe	--	flyash (Ca rich)	

Appendix Table 18. Particles observed on the center portion of stage 5 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	0.7	Si,Al	--	--	clay	
2	1.2	Si	--	--	quartz	
3	0.6	Fe	--	--	iron (oxide)	
4	0.5	Si,Al	Fe	--	clay	
5	0.4	Si	--	--	quartz	
6	1.3	Fe	--	--	iron (oxide)	
7	0.4	Pb	--	--	lead (oxide)	
8	0.8	Pb,Br	--	--	lead bromochloride	
9	0.6	Si,Al	--	--	clay	
10	0.8	Si	--	--	quartz	
11	0.7	Si,Al	--	Fe	flyash (Si rich)	
12	0.7	Pb,Br	--	--	lead bromochloride	
13	0.9	Si,Al,S	--	--	clay (w/sulfur)	
14	0.9	--	--	--	carbon	
15	0.5	Si	--	--	quartz	
16	1.2	Si,Fe	Al	--	aluminum silicate, iron	
17	0.8	Si	Al,Fe	--	clay	
18	0.7	Ca	Al,Si,P,S,Fe	--	flyash (Ca rich)	
19	0.5	Fe	--	--	iron (oxide)	
20	0.7	--	--	--	flyash (carbon)	[see Appendix Table 17]
21	0.4	Pb,Br	Cl	--	lead bromochloride	
22	0.4	Si,Al	--	--	clay	
23	0.8	Si	Al,Fe,K,S	--	clay	
24	1.2	Ca	--	--	mineral calcium	calcite
25	0.6	Si	--	Mg,Ca,Fe	flyash (Si rich)	
26	0.9	Si	--	--	quartz	
27	0.7	Fe,Zn	Pb,K,Al,Si	--	flyash (metal rich)	
28	0.4	Pb	Br	--	flyash (lead rich)	
29	1.4	Si	--	--	quartz	
30	1.2	--	--	Al,Si,Pb/S,Cl	auto emission	
31	0.8	Pb,Br	--	--	lead bromochloride	
32	0.6	Si	Al,K,Ca,Fe	--	flyash (Si rich)	
33	1.1	Si	--	--	quartz	

Appendix Table 19. Particles observed on the outer portion of stage 6 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle	Elements			Particle Type	Comments
	Effective Diameter (μ m)	Major	Moderate	Trace		
1	2.8	--	S, K, Zn	Al, Si, Cl, Ca	auto emission	no lead Mn peak (1) associated  no areas of elemental concentration
2	1.0	--	Pb, Br	Cr, Mn, Fe	auto emission	
3	1.1			--		
4	0.3	Si	--	Al, Pb/S	quartz	
5	0.5	Fe	--	Si	iron (oxide)	
6	1.2	Si, Al	--	Pb/S, Fe	clay	
7	0.9	--	--	--	carbon	
8	1.1	Si	Al, K, Ca, Fe	--	clay	
9	0.6	Si	Al, K	--	aluminum silicate, potassium flyash (metal rich)	
10	0.2	Mn, Fe	--	--	flyash (Si rich)	no areas of elemental concentration
11	0.2	Si	Al, K, Ca, Fe	--	quartz	
12	0.4	--	Si	--	auto emission	
13	4.0	--	--	Pb/S, Al/Br	auto emission	
14	1.1	--	--	Pb/S, Al/Br, Si	auto emission	
15	1.1	--	--	--	auto emission	
16	0.9	S, Ca, Cl	--	--	calcium salt	
17	1.1	--	--	Si, S/Pb	carbon (soot)	
18	0.4	Pb/Br	--	--	lead bromochloride	
19	1.5	--	--	--	auto emission	embedded in #29 embedded in #29 embedded in #30
20	0.8	--	--	Pb/S, Si, Al/Br, Fe	auto emission	
21	0.4	--	S, Zn	zinc/sulfur salt		
22	0.4	--	Al, Si, Pb, S, Ca	--	aluminum silicate, calcium auto emission	
23	1.5	--	--	--	carbon (soot)	
24	0.5	--	--	Pb/S, K	lead bromochloride	
25	0.3	Pb, Br	--	Fe, Zn	phosphate	
26	0.8	P	--	S	lead bromochloride	
27	0.8	Pb, Br	--	--	quartz	
28	0.6	Si	--	--	auto emission	embedded in #32
29	2.0	--	--	Pb/S	auto emission	
30	1.2	--	--	--	quartz	
31	0.3	--	Si	--		embedded in #32

Appendix Table 20. Particles observed on the middle portion of stage 6 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle	Elements			Particle Type	Comments
	Effective Diameter (μ m)	Major	Moderate	Trace		
1	1.2	--	--	--	auto emission	
2	0.3	--	Al, Si, Ca	--	aluminum silicate, calcium	possible flyash
3	0.4	Pb, Br, Cl	--	--	lead bromochloride	associated with #23
4	0.3	--	Zn	Pb, Cl, Br	metal	associated with #23
5	0.7	Al, Si, S, Fe	--	K, Ca	clay	embedded in #23
6	0.4	Pb, Br, Cl	--	Si	lead bromochloride	embedded in #23
7	0.6	Mn	--	Al, Si, Pb/S	metal	embedded in #23
8	0.5	Pb, K	--	Cl, Fe, Zn, P	unknown	embedded in #23
9	0.6	Pb, Br	--	--	lead bromochloride	embedded in #23
10	0.9	Si	Al, K, Ca, Fe	--	flyash (Si rich)	embedded in #23
11	0.3	Pb, Si	--	--	flyash (metal rich)	
12	1.3	--	--	Pb/S, Si, Al/Br, Fe	auto emission	
13	0.3	Pb, Fe, Zn	Si	--	metal	embedded in amorphous mass
14	0.2	--	--	Mn	carbon w/metal	
15	0.3	Zn, S	--	--	zinc-sulfur salt	
16	0.3	Pb, Br	--	Fe, Cl	lead bromochloride	
17	2.2	--	--	Pb/S	auto emission	
18	2.9	--	--	Pb/S, Zn, Al/Br	auto emission	
19	2.6	--	--	Pb/S, Al/Br, Cl, Zn	auto emission	
20	3.5	--	--	Pb/S, Zn		
21	1.1	Ca	--	Al, P	flyash (Ca rich)	
22	1.3	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
23	3.8	--	--	--	auto emission	

Appendix Table 21. Particles observed on the center portion of stage 6 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	1.1	Si, Al	--	Fe	flyash (Si rich)	
2	3.6	--	Pb	--	auto emission	
3	0.6	Si	Al, K, Ca, Fe	--	flyash (Si rich)	
4	0.7	Mg	S, Cl	Si, Al, Cr	unknown mineral	
5	0.3	--	Si, S	--	flyash (Si rich)	
6	0.3	--	Cl	Pb/S	salt	
7	0.3	--	Ca, P, Al, Si	--	unknown mineral	possibly sodium chloride
8	1.6	--	--	--	auto emission	
9	0.6	--	--	--	auto emission	
10	0.7	Pb, Br, Cl	--	--	lead bromochloride	
11	1.3	--	--	Pb, Br, Zn	auto emission	
12	0.4	--	--	Ca	calcium mineral	
13	0.6	Zn	S, Cl	--	zinc salt	embedded in #16
14	0.4	--	Pb, Br, Cl	--	auto emission	embedded in #16
15	0.9	Si, Al	Fe	--	flyash (Si rich)	embedded in #16
16	3.5	--	--	Pb, Cl, Zn	auto emission	
17	1.3	--	--	Pb, Cl, Zn	auto emission	
18	0.3	--	--	--	carbon	
19	1.4	--	--	--	auto emission	embedded in #19
20	1.5	--	--	Zn	auto emission	
21	3.10	--	--	Pb	auto emission	
22	0.9	Fe	Si, Al	--	flyash (Fe rich)	
23	0.8	Pb	--	Fe	lead (oxide)	
24	0.6	--	--	--	carbon	

Appendix Table 22. Particles observed on the outer portion of stage 7 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	2.3	--	--	Pb	auto emission	
2	1.2	--	--	Cr, S, Zn	auto emission	
3	1.9	--	--	Pb/S, Br/Al	auto emission	
4	0.4	--	--	S	auto emission	
5	0.6	S	--	Zn	auto emission	
6	0.6	--	--	Pb/S	auto emission	embedded in #4
7	1.5	--	S	Pb/S, Zn	auto emission	
8	0.4	--	--	S, Zn	auto emission	
9	0.2	--	--	S	auto emission	
10	0.3	--	--	S	auto emission	
11	0.3	--	--	S	auto emission	
12	0.4	--	--	S	auto emission	
13	0.2	--	--	Pb/S, Cl, Al/Br	auto emission	
14	1.0	--	--	S	auto emission	
15	0.1	--	--	Si, S	auto emission	
16	0.1	--	--	S	auto emission	
17	0.4	--	--	S	auto emission	
18	0.9	Pb, K	--	Al/Br	unknown	
19	0.4	--	--	Pb/S, Al/Br	auto emission	embedded in #22
20	0.1	--	--	Si, Pb/S	auto emission	
21	0.2	--	--	--	auto emission	
22	1.4	--	--	--	auto emission	
23	4.6	--	Pb, Br	--	auto emission	
24	0.7	Si, Al, K	--	Pb, Zn, Fe	aluminum silicate, potassium	numerous spots with stronger fluorescence
25	0.4	Si, Pb, Ca	--	Fe, K, Cl, Al	auto emission	
26	0.3	--	--	Fe	auto emission	
27	0.9	--	--	Cr	auto emission	
28	0.5	Si, Pb, S, Ca, Fe	--	Zn, Al, K	flyash (metal rich)	

Appendix Table 23. Particles observed on the middle portion of stage 7 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	4.5	--	--	Pb/S	auto emission	
2	0.2	--	--	Al, Pb/S, K, Ca, Fe	flyash (?)	
3	0.2	--	--	--	flyash (?)	
4	0.3	--	--	--	flyash (?)	
5	0.5	--	--	--	flyash (?)	
6	0.2	--	--	Pb/S	flyash (?)	
7	0.2	--	--	Pb/S, Al/Br, Si	flyash (?)	
8	0.3	--	Pb	Al/Br, Cl	flyash (?)	
9	0.5	--	S	Al, Mg	auto emission	
10	0.15	--	S	--	flyash (?)	
11	0.3	--	--	Pb/S	auto emission	
12	--	S	--	Al/Br, Si	--	selected area of #1
13	--	Pb, Br	P, Cl, Si	--	--	selected area of #1
14	0.2	Pb	--	Al/Br, Si, Cl, Ca, Fe, Zn	auto emission	
15	0.4	--	--	Pb/S, Al/Br, Si	auto emission	
16	0.4	S	--	Al, K	soot	
17	0.2	S	--	Al, K	soot	
18	0.3	Pb	--	Al/Br, Si, Cl	auto emission	
19	0.8	--	--	--	auto emission	
20	0.5	--	--	--	auto emission	

Note: Particles 2-15 associated w/#1 - Flyash (?), distinct spherical morphology

Appendix Table 24. Particles observed on the middle portion of stage 7 of the Andersen 8-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle	Elements			Particle Type	Comments
	Effective Diameter (μ m)	Major	Moderate	Trace		
Area with relatively high Pb/S peak, selected areas and embedded particles						
1	1.8	Si	S	Al, K, Ca, Fe, Zn, Pb	quartz	particle
2	1.5	Ca, Si, S	Fe, Br	Pb	flyash (Ca rich)	particle
3	1.1	Pb, Br, Ca	Si, Fe, Zn	--	auto emission	particle
4	--	Pb, Si, Br/Al	Fe, Zn, K, Ca	Cr, Mn, Mg	auto emission	area
5	--	Pb, Si, Al/Br	Cl, K, Ca, Fe, Zn	Ti, Mn, Mg, P	auto emission	area

Note: Matrix area made up of small particles which appear spherical.

Area with relatively low Pb/S near center of spot

1	0.4	Si, S	K, Ca, Fe, Pb, Zn, Al	Ti, Mn, Cl, Br	area fluorescence
2	0.4				
3	0.2				
4	0.6				
5	0.7				
6	0.5				
7	0.6				
8	0.4				
9	0.6				
10	0.4				
11	0.3				

Appendix Table 25. Particles observed on the outer portion of the backup stage of the Andersen 6-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	15.0	S	Si	--	auto emission	
2	n/a	--	--	--	--	
3	8.6	--	S,Pb	Ca,K,Cr/Nd,Fe,Cl	auto emission	
4	4.1	Si	Al,K,Ca,Fe	--	clay	
5	5.1	Si	Al,K,Ca,Fe	--	clay	
6	2.1	Si	--	--	quartz	
7	4.2	S	Al,Fe	Ca	clay	
8	5.1	--	S,Pb	Si,K,Cl	auto emission	
9	3.4	Si,Al	K	Fe	aluminum silicate, potassium	
10	8.5	S	Pb	Al,Si,K,Ca,Mg	auto emission	
11	11.2	S	Pb	Mg,Si,Cl,K,Ca	auto emission	
12	18.6	S	K,Ca	Mg,Si	auto emission	
13	4.5	Si	--	Fe,Al	quartz	
14	2.3	Si	--	K,Fe	quartz	
15	10.2	S,Pb	--	Cl,Ca	auto emission	
16	8.5	--	S	Cl,K,Si,Mg	auto emission	
17	7.6	--	S,Pb	Cl,Si,Mg	auto emission	
18	11.0	S	Si,K,Ca	Mg,Fe	auto emission	
19	2.8	Ca,Al	Ti,Fe	Mg,Si	flyash (Ca rich)	
20	4.2	S	--	Pb,Si,Mg,Fe	auto emission	
21	6.8	Si	Al	K,Ca,Fe,Mg	clay	
22	5.9	--	S,Pb	Br,Cl	auto emission	
23	4.4	Si,Al	K	Fe	aluminum silicate, potassium	
24	5.0	--	S	Al,Cl,K,Mg	auto emission	
25	6.8	--	S,Pb	K,Mn,Fe,Si,Al,Cl,Mg,K,Ca	auto emission	

Appendix Table 26. Particles observed on the middle portion of the backup stage of the Andersen 6-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	13.2	--	S	Pb,Cl,Ca,Al,Si,Fe,Zn	auto emission	
2	18.7	--	S	Si,Al,K,Ca,Cl	auto emission	
3	13.4	--	S	Pb,Si,Fe,Mg,Al	auto emission	
4	2.2	Si	Al,K,Ca,Fe	S	clay	
5	3.1	Si	Al	Ca	clay	
6	5.4	Si	K,Al	--	aluminum silicate, potassium	
7	5.9	--	S	Pb,Cl,Si,Al	auto emission	
8	7.4	--	S	Pb,Si,K,Fe	auto emission	
9	4.4	Ca	Si,Fe	S,Cl,K,Al	mineral calcium	
10	5.9	--	S	Al,Cl,K	auto emission	
11	4.5	--	Si,S	Cl,Fe,Zn	auto emission	
12	4.0	Si,Al	K,Ca,Fe	S	clay	
13	5.9	--	S	Ca,Si	auto emission	
14	15.3	--	S,Si	--	auto emission	
15	2.7	Si	Al,Ti,Fe	K	clay	
16	4.5	Si	Al,Fe	K,Ca	clay	
17	6.4	--	--	--	clay	
18	20.6	--	S	Pb,Si,Cl,K	auto emission	
19	6.8	Al	--	Zn	contaminant (not used)	
20	1.4	Si	Al,Ca	Pb/S	aluminum silicate, calcium	
21	4.5	--	Si,S	Al,Fe,Cl	auto emission	
22	5.4	--	S	Pb,Si,K,Ca,Fe	auto emission	
23	1.9	--	Si,S	Cl,Ca	auto emission	
24	3.9	--	Si,S	Cl,Ca,Fe,Zn	auto emission	
25	3.9	--	Si,S	Pb,Zn,Fe,Mn,Co	auto emission	
26	5.3	Si	Al,K,Ca,Fe	--	clay	
27	4.4	--	S,Si	Pb,K,Cl,Mg,Pb,Mn,Fe	auto emission	
28	4.8	Si	--	--	quartz	
29	3.8	Si	Al,K,Ca,Fe	--	clay	
30	6.6	--	S	Si,Pb,Al	auto emission	
31	5.4	--	--	Pb/S,Si	auto emission	
32	5.9	--	--	Pb/S,Si	auto emission	
33	4.5	--	S	Si	auto emission	
34	4.5	--	S	Si	auto emission	
35	1.8	Si	Al,K,Ca,Fe	--	clay	
36	2.0	Si	Al,K,Ca,Fe	--	flyash (Si rich)	

Appendix Table 27. Particles observed on the center portion of the backup stage of the Andersen 6-stage impactor from the Trout Farm location, November 13, 1973

No.	Particle Effective Diameter (μ m)	Elements			Particle Type	Comments
		Major	Moderate	Trace		
1	4.7	Si	K,Al	--	aluminum silicate, potassium	
2	2.8	Si	Al,K,Ca,Fe	--	flyash (Si rich)	
3	7.1	--	S,Si	I	auto emission	
4	2.3	Si	--	--	quartz	
5	5.7	--	--	Si,S	auto emission	
6	5.5	Si	Al,K,Fe	--	aluminum silicate, potassium	
7	9.3	--	S,Si	K	auto emission	
8	10.4	--	S	Si	auto emission	
9	3.0	Ag	--	Si	(Contaminant)	
10	5.0	--	S	Si	auto emission	
11	3.0	P,Fe	--	--	mineral phosphate	
12	6.0	--	S/Pb	Si	auto emission	
13	9.6	Si	Al,K,Ca,Fe	--	clay	
14	6.2	Si	Al,K	Fe	aluminum silicate, potassium	
15	7.0	Si,Ca	Al,Fe	--	aluminum silicate, calcium	
16	3.8	Si,Al,Ca	Fe	--	aluminum silicate, calcium	
17	9.3	--	S	Si	auto emission	
18	6.0	S	K,Ca	--	sulfur mineral	
19	19.0	Ca,K,Cl	S,Si	--	unknown	possibly tire particle
20	9.3	S	Si	--	auto emission	
21	6.7	--	S	Si	auto emission	
22	3.2	Si,Al,Ca	Fe	--	flyash (Ca rich)	
23	3.7	P	Si	--	mineral phosphate	
24	5.9	Si	--	--	quartz	
25	3.5	--	--	--	auto emission	
26	2.9	--	S,Si	K	auto emission	
27	5.0	Al,Si	Ca	Fe	Al,Si,Ca	
28	7.7	--	S	Si	auto emission	
29	2.8	Ca,Al,Si	Fe	--	Al,Si,Ca	
30	9.0	--	S	Si	auto emission	
31	9.8	S	Si	--	auto emission	
32	2.8	Pb	Al/Br,Cl	--	PbBrCl	
33	3.8	Si	Al,Ca	Fe	clay	

Appendix Table 26. Size summary of mineral aerosols observed on stage β of the 16 Nov. 1973 Trout Farm 5-stage Anderson impactor

Stage-Area	Quartz	Aluminum Silicates					Calcium/ Sulfur	Rutile	Other	Total
		Clay	Potassium	Calcium	Iron	Other				
β -Outer	D_g	5.3	6.6	8.0	3.8	6.0	2.0			6.2
	S_g	0.8	4.7	3.9	--	0.8	--			3.6
	n	4	8	4	1	2	1			20
	ΣD_g	21.0	52.9	31.9	3.8	11.9	2.0			123.5
β -Middle	D_g	7.4	5.6	4.6	5.5		9.4			5.7
	S_g	2.6	4.4	4.1	3.5		--			3.8
	n	3	10	5	5		1			24
	ΣD_g	22.3	55.6	23.2	27.3		9.4			137.8
β -Center	D_g	6.7	7.5	7.0			4.0		9.8	7.2
	S_g	3.1	3.2	1.0			--		--	2.7
	n	6	13	6			1		1	27
	ΣD_g	40.3	97.5	41.7			4.0		9.8	193.3
Total	D_g	6.4	6.6	6.5	5.2	6.0	6.7		9.8	6.4
	S_g	2.5	4.0	3.2	3.2	0.8	2.0		--	3.4
	n	13	31	15	6	2	1		1	71
	ΣD_g	83.6	206.0	96.8	31.1	11.9	13.4		9.2	454.6

D_g = mean effective diameter (μm)

S_g = standard deviation

n = number observed

ΣD_g = sum of effective diameters

Appendix Table 29. Size summary of mineral aerosols observed on stage 1 of the 16 Nov. 1973 Iron: Farm 5-stage Anderson impactor:

MINERALS										
Stage-Area	Aluminum Silicates						Calcium/ Sulfur	Rutile	Other	Total
	Quartz	Clay	Potassium	Calcium	Iron	Other				
1-Outer	D _g 5.4	6.1	7.8	4.6		5.0				5.8
	S _g 2.0	3.9	6.0	0.6		--				3.7
	n 4	18	4	3		1				33
	ΣD _g 21.4	110.2	31.2	13.4		5.0				191.5
1-Middle	D _g 4.7	6.2	5.3			3.7				5.5
	S _g 2.7	3.6	1.6			--	2.8			3.0
	n 6	17	6			1	1.8			33
	ΣD _g 28.1	105.3	31.9			3.7	5.6			180.2
1-Center	D _g 4.5	4.7	4.5	3.7	7.1	3.1			12.9	4.9
	S _g 1.9	3.2	2.2	0.4	3.6	--			--	3.0
	n 6	32	13	2	4	1			1	59
	ΣD _g 26.8	150.6	56.3	7.3	28.4	3.1			12.9	287.4
Total	D _g 4.8	5.5	5.3	4.1	7.1	3.9			12.9	5.3
	S _g 2.2	3.5	3.2	0.6	3.6	1.0	2.8		--	3.2
	n 16	67	22	5	4	3	1.8		1	124
	ΣD _g 76.3	366.1	121.4	20.7	28.4	11.8	5.6			699.1

D_g = mean effective diameter (μm)

S_g = standard deviation

n = number observed

ΣD_g = sum of effective diameters

Appendix Table 30. Size summary of mineral aerosols observed on stage 2 of the 16 Nov. 1973 Trout Farm E-stage
Anderson impactor

Stage-Area	MINERALS									
	Aluminum Silicates									
	Quartz	Clay	Potassium	Calcium	Iron	Other	Calcium/ Sulfur	Rutile	Other	Total
2-Outer	D_g	6.2	6.0	4.8	6.0		1.8	2.7		5.7
	S_g	3.2	3.1	1.7	--		--	--		2.8
	n	6	12	9	1		1	1		30
2-Middle	ΣD_g	36.9	82.5	43.6	6.0		1.8	2.7		173.5
	D_g	4.3	4.3	4.3	5.4	4.0	5.1			4.5
	S_g	1.2	2.2	--	--	--	0.3			1.5
2-Center	n	4	9	1	1	1	3			20
	ΣD_g	17.2	34.5	4.3	5.4	4.0	15.9			90.4
	D_g	5.1	7.0	6.6	6.2		5.0			6.4
Total	S_g	0.5	1.5	2.7	2.8		--			2.1
	n	3	9	6	5		1			24
	ΣD_g	15.1	62.6	39.6	31.2		5.0			133.7
Total	D_g	5.3	6.1	5.5	6.1	4.0	5.1	2.7		5.6
	S_g	2.3	2.6	2.2	2.3	--	1.6	--		2.3
	n	13	30	16	7	1	5	1		74
Total	ΣD_g	69.4	183.6	87.5	42.6	4.0	22.7	2.7		417.6

D_g = mean effective diameter (μm)

S_g = standard deviation

n = number observed

ΣD_g = sum of effective diameters

Appendix Table 31. Size summary of mineral aerosols observed on stage 3 of the 16 Nov. 1973 Trout Farm E-stage, Anderson impactor

Stage-Area	MINERALS									
	Aluminum Silicates					Calcium/Sulfur				
	Quartz	Clay	Potassium	Calcium	Iron	Other	Calcium	Antile	Other	Total
3-Outer	D _e	1.4	1.1	2.1	0.8	0.8	2.0			1.4
	S _e	0.8	0.5	1.2	--	0.5	--			0.9
	n	4	7	5	1	2	1			20
	ΣD _e	5.5	7.4	10.5	0.8	1.5	2.0			27.7
3-Middle	D _e	1.8	1.9	1.2	1.3	2.3	1.9	0.8	1.8	1.8
	S _e	0.9	1.3	1.0	0.1		0.5	--	--	1.1
	n	7	23	5	2	1	4	1	1	44
	ΣD _e	12.4	44.5	5.9	2.6	2.3	7.7	0.8	1.8	78.0
3-Center	D _e	2.5	2.0	3.0	2.4		2.3	1.4	2.3	2.2
	S _e	0.4	0.9	1.1	0.9		0.3	--	0.3	0.8
	n	4	21	4	2		3	1	2	37
	ΣD _e	9.9	41.4	11.8	4.7		6.9	1.4	4.6	80.7
Total	D _e	1.9	1.9	2.0	1.6	1.3	2.1	1.1	2.1	1.9
	S _e	0.8	1.1	1.3	1.0	1.0	0.4	0.4	0.4	1.0
	n	15	51	14	5	3	8	2	2	101
	ΣD _e	27.8	93.3	28.2	8.1	3.8	16.6	2.2	6.4	186.4

D_e = mean effective diameter (μm)

S_e = standard deviation

n = number observed

ΣD_e = sum of effective diameters

Appendix Table 32. Size summary of mineral aerosols observed on stage 4 of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

Stage-Area	MINERALS										
	Aluminum Silicates										
	Quartz	Clay	Potassium	Calcium	Iron	Other	Calcium	Calcium/ Sulfur	Rutile	Other	Total
1-Outer	D _e	1.0	1.3	1.4		0.8	1.6	1.1		1.3	1.3
	S _e	0.2	0.5	0.5		--	0.4	0.4		0.5	0.4
	n	3	13	7	1	4	4			2	34
	ΣD _e	2.9	16.3	9.5		0.8	6.2	4.5		2.5	42.7
4-Middle	D _e	1.8	1.4	1.2	0.7				0.9		1.3
	S _e	--	1.0	0.6	0.1				0.5		0.9
	n	1	16	3	2				2		24
	ΣD _e	1.8	22.9	3.7	1.3				1.7		31.4
4-Center	D _e	0.8	1.4	1.5	1.7	0.9	1.8	1.7		1.3	1.4
	S _e	0.6	1.1	0.7	1.2	--	--	0.6		0.8	0.9
	n	3	15	7	4	1	1	2		3	36
	ΣD _e	2.4	20.6	10.4	6.6	0.9	1.8	3.3		3.9	49.9
Total	D _e	1.0	1.4	1.4	1.3	0.9	1.6	1.3		1.3	1.3
	S _e	0.5	0.9	0.6	1.1	0.1	0.3	0.5		0.7	0.8
	n	7	44	17	6	2	5	6		5	94
	ΣD _e	7.1	59.8	23.6	7.9	1.7	8.0	7.8		6.4	124.0

D_e = mean effective diameter (μm)

S_e = standard deviation

n = number observed

ΣD_e = sum of effective diameters

Appendix Table 33. Size summary of mineral aerosols observed on stage 5 of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

<u>Stage-Area</u>	<u>Aluminum Silicates</u>						<u>Calcium/ Sulfur</u>	<u>Rutile</u>	<u>Other</u>	<u>Total</u>
	<u>Quartz</u>	<u>Clay</u>	<u>Potassium</u>	<u>Calcium</u>	<u>Iron</u>	<u>Other</u>				
5-Outer	D _c	0.8					0.5			0.8
	S _e	0.7		--	0.6		0.1			0.7
	n	9	17	1	9		2			39
	ΣD _e	7.4	16.2	0.5	5.8		1.0			31.4
5-Middle	D _e	1.0	1.4			1.1				1.2
	S _e	0.7	1.1			0.6				0.8
	n	4	4			3				11
	ΣD _e	3.9	5.5			3.3				12.7
5-Center	D _e	0.9	0.7			1.2				0.8
	S _e	0.4	0.2			--				0.3
	n	7	7			1				16
	ΣD _e	6.3	4.7			1.2				13.4
Total	D _e	0.9	0.9	0.5	0.6	1.1				0.9
	S _e	0.6	0.8	--	0.3	0.5				0.5
	n	20	28	1	9	4				66
	ΣD _e	17.6	26.4	0.5	5.8	4.5				57.5

$\bar{D}_e$ = mean effective diameter (μ m)
 s_e = standard deviation
 n = number observed
 ΣD_e = sum of effective diameters

Appendix Table 34. Size summary of mineral aerosols observed on stage 6 of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

Stage-Area	MINERALS									
	Aluminum Silicates									
	Quartz	Clay	Potassium	Calcium	Iron	Other	Calcium	Calcium/ Sulfur	Rutile	Other
6-Outer	D _e	0.4	1.2	0.6	0.4					
	S _e	0.1	0.1	--	--					
	n	4	2	1	1					
	ΣD _e	1.6	2.3	0.6	0.4					
6-Middle	D _e		0.7		0.3					
	S _e		--		--					
	n		1		1					
	ΣD _e		0.7		0.3					
6-Center	D _e						0.4			
	S _e						--		0.5	0.5
	n						1		0.3	0.2
	ΣD _e						0.4		2	3
Total	D _e	0.4	1.0	0.6	0.4		0.4		1.0	1.4
	S _e	0.1	0.3	--	0.1		--		0.5	0.6
	n	4	3	1	2		1		0.3	0.3
	ΣD _e	1.6	3.0	0.6	0.7		0.4		2	13
	D _e								1.0	1.0
	S _e									
	n									
	ΣD _e									7.3

Appendix Table 35. Size summary of mineral aerosols observed on the backup filter of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

<u>Stage-Area</u>	<u>Quartz</u>	<u>Minerals</u>						<u>Sulfur</u>	<u>Other</u>	<u>Total</u>
		<u>Clay</u>	<u>Potassium</u>	<u>Calcium</u>	<u>Iron</u>	<u>Other</u>	<u>Calcium</u>			
B-1	D _E	3.0	5.1							4.3
	S _E	1.3	0.7							1.3
	n	3	2							9
	ΣD _E	8.9	7.4							36.9
B-2	D _E	4.8	5.4	1.4			4.4			3.2
	S _E	--	--	--			--			1.6
	n	1	1	1			1			12
	ΣD _E	4.8	5.4	1.4			4.4			38.1
B-3	D _E	4.1	5.8	4.7				6.0	3.4	5.0
	S _E	2.5	1.0	1.8				--	0.5	2.0
	n	2	3	4				1	2	14
	ΣD _E	8.2	13.4	18.6				6.0	6.7	70.3
Total	D _E	3.7	5.1	4.0			4.4	6.0	3.4	4.2
	S _E	1.5	1.2	2.1			--	--	0.5	1.9
	n	6	6	5			--	1	2	35
	ΣD _E	21.9	30.6	20.0			4.4	6.0	6.7	145.3

D_f = mean effective diameter (μm)

 σ_T = standard deviation

n = number observed

ΣD_p - sum of effective diameters

Appendix Table 36. Size summary of flyash, salt, lead, metal and carbon aerosols observed on stage ϕ of the 16 Nov. 1973 Trout Farm 8-stage Anderson Impactor

Stage-Area	Flyash ¹			Lead Compound			Carbon		
	Si-rich	Ce-rich	Metal-rich	Pb	PbBrCl(s)	Metal	Salt	Particles	Auto Emission
ϕ -Outer	D_g	1.6	--	--	1.6	--	--	--	3.9
	S_g	1.0	--	--	1.0	--	--	--	0.0
	n	22	--	--	22	--	--	--	2
	ΣD_g	34.8	--	--	34.6	--	--	--	7.8
ϕ -Middle	D_g	2.8	1.6	--	2.4	--	--	--	5.0
	S_g	2.0	0.2	--	1.7	--	--	--	--
	n	6	3	--	9	--	--	--	1
	ΣD_g	16.8	4.8	--	21.6	--	--	--	5.0
ϕ -Center	D_g	3.3	2.7	--	2.9	4.1	--	--	--
	S_g	2.8	1.2	--	1.8	1.8	--	--	--
	n	4	7	--	11	2	--	--	--
	ΣD_g	13.1	18.8	--	31.9	8.2	--	--	--
Total	D_g	2.0	2.4	--	2.1	4.1	--	--	--
	S_g	1.6	1.1	--	1.5	1.8	--	--	--
	n	32	10	--	42	2	--	--	--
	ΣD_g	64.7	23.6	--	88.3	8.2	--	--	--

D_g = mean effective diameter (μm)

S_g = standard deviation

n = number observed

ΣD_g = sum of effective diameters

Appendix Table 37. Size summary of flyash, salt, lead, metal and carbon aerosols observed on stage 1 of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

Stage-Area	Flyash			Lead Compound			Carbon		
	Si-rich	Ca-rich	Metal-rich	Total	Pb	PbBrCl(S)	Metal	Salt	Particles
1-Outer	$\bar{D}_e$	--	--	--	--	--	--	--	2.3
	S_e	--	--	--	--	--	--	--	--
	n	--	--	--	--	--	--	--	1
1-Middle	ΣD_e	--	--	--	--	--	--	--	2.3
	$\bar{D}_e$	2.6	2.2	--	2.3	--	--	--	--
	S_e	1.4	1.0	--	1.1	--	--	--	--
1-Center	n	2	6	--	8	--	--	--	--
	ΣD_e	5.2	13.3	--	18.5	--	--	--	--
	$\bar{D}_e$	1.1	--	--	1.1	--	--	--	1.6
Total	S_e	0.7	--	--	0.7	--	--	--	--
	n	2	--	--	2	--	--	--	1
	ΣD_e	2.2	--	--	2.2	--	--	--	1.6
Total	$\bar{D}_e$	1.9	2.2	--	2.1	--	--	--	1.6
	S_e	1.3	1.0	--	1.1	--	--	--	--
	n	4	6	--	10	--	--	--	1
Total	ΣD_e	7.4	13.3	--	20.7	--	--	--	1.6
	$\bar{D}_e$	--	--	--	--	--	--	--	--
	S_e	--	--	--	--	--	--	--	--
	n	--	--	--	--	--	--	--	--

$\bar{D}_e$ = mean effective diameter (μm)

S_e = standard deviation

n = number observed

ΣD_e = sum of effective diameters

Appendix Table 38. Size summary of flyash, salt, lead, metal and carbon aerosols observed on stage 2 of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

Stage-Area	Flyash				Lead Compound			Carbon		
	Si-rich	Ce-rich	Metal-rich	Total	Pb	PbBrCl(g)	Metal	Salt	Particles	Auto Emission
2-Outer	D_g	2.6	3.6	--	3.1					
	S_g	1.1	1.3	--	1.1					
	n	2	2	--	4					
2-Middle	ΣD_g	5.1	7.1	--	12.2					
	D_g	3.1	2.3	--	2.4				9.6	
	S_g	1.2	1.9	--	1.2				6.2	
2-Center	n	4	13	--	17				2	
	ΣD_g	12.2	29.4	--	41.6				19.2	
Total	D_g	1.8	2.3	1.7	2.0				3.7	
	S_g	0.6	1.5	0.1	1.1				0.7	
	n	13	14	2	24				3	
	ΣD_g	23.4	31.5	3.4	58.3				11.2	
Total	D_g	2.1	2.3	1.7	2.2				6.1	
	S_g	0.9	1.6	0.1	1.2				4.5	
	n	19	29	2	50				5	
	ΣD_g	40.7	68.0	3.4	112.1				30.4	

D_g = mean effective diameter (μm)

S_g = standard deviation

n = number observed

ΣD_g = sum of effective diameters

Appendix Table 39. Size summary of flyash, salt, lead, metal and carbon aerosols observed on stage 3 of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

Stage-Area	Flyash			Lead Compound			Carbon				
	Si-rich	Ca-rich	Metal-rich	Total	Pb	Pb:Cl(S)	Metal	Salt	Particles	Auto Emission	Organic Species
3-Outer	D _f	1.4		1.4			0.3				
	S _f	--		--			1(1)				
	n	1		1			0.3				
	ΣD _f	1.4		1.4							
3-Middle	D _f	1.6	1.4	1.5	1.0	1.0			2.0	5.8	
	S _f	0.9	0.6	0.8	--	--			0.8	--	
	n	5	2	7	1	1			4	1	
	ΣD _f	7.9	2.8	10.7	1.0	1.0			7.8	5.8	
3-Center	D _f	1.8	1.4	1.7			2.4				
	S _f	1.3	0.7	1.1			1(2)				
	n	6	2	8			2.4				
	ΣD _f	11.0	2.8	13.8							
Total	D _f	1.7	1.4	1.6	1.0	1.0	1.4		2.0	5.8	
	S _f	1.1	0.5	0.9	--	--	1.5		0.8	--	
	n	11	5	16	1	1	2		4	1	
	ΣD _f	18.9	7.0	25.9	1.0	1.0	2.7		7.8	5.8	

D_g = mean effective diameter (μm)

S_g = standard deviation

n = number observed

ΣD_g = sum of effective diameters

(1) Iron

(2) Aluminum

Appendix Table 40. Size summary of flyash, salt, lead, metal and carbon aerosols observed on stage 4 of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

Stage-Area	Flyash				Lead Compound			Carbon		
	St-rich	Ca-rich	Metal-rich	Total	Pb	PbBrCl(S)	Metal	Salt	Particles	Auto Emission
4-Outer	D _g	1.1	1.0	0.9	0.7	0.9	0.9	0.9	1.2	
	S _g	0.1	0.5	--	--	0.4	--	--	0.4	
	n	7	5	1	1	2	1	1	4	
	ΣD _g	7.8	5.1	0.9	0.7	1.8	0.9	0.6	4.7	
4-Middle	D _g	1.0	0.9	1.0						
	S _g	0.4	0.4	0.4						
	n	12	3	15						
	ΣD _g	12.5	2.6	15.1						
4-Center	D _g	1.0	1.2	1.0	1.1				1.8	
	S _g	--	0.1	--	0.1				--	
	n	1	2	1	4				1	
	ΣD _g	1.0	2.3	1.0	4.30				1.8	
Total	D _g	1.1	1.0	1.0	0.7	0.9	0.9	0.8	1.2	
	S _g	0.3	0.4	0.1	--	0.4	--	--	0.4	
	n	20	10	2	32	2	1	1	4	
	ΣD _g	21.3	10.0	1.9	33.2	0.7	1.6	0.6	4.7	

D_g = mean effective diameter (μm)

S_g = standard deviation

n = number observed

ΣD_g = sum of effective diameters

Appendix Table 41. Size summary of flyash, salt, lead, metal and carbon aerosols observed on stage 5 of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

Stage-Area	Flyash				Lead Compound				Carbon			
	Si-rich	Ca-rich	Metal-rich	Total	Pb	PbBrCl(8)	Metal	Salt	Particles	Auto Emission	Organic Species	
5-Outer	D_g	1.4	0.7	1.0	0.3	0.6	0.5	0.9	0.4	0.7		
	S_g	0.8	0.1	0.7	--	0.3	0.1	0	0.1	--		
	n	2	2	4	1	17	6	2	2	1		
5-Middle	ΣD_g	2.8	1.3	4.1	0.3	10.2	2.9	1.8	0.7	0.7		
	D_g	0.6	0.6	0.6	0.4	0.7	0.4	1.2	0.6	0.6		0.7
	S_g	0.1	0.2	0.1	--	0.5	--	--	0.3	--		0.1
5-Center	n	6	4	10	1	3	1	1	3	1		3
	ΣD_g	3.7	2.3	6.0	0.4	2.1	0.4	1.2	1.8	0.6		2.1
	D_g	0.6	0.7	0.6	0.4	0.7	0.8		0.9	1.2		0.7
Total	S_g	0.1	--	0.1	--	0.2	0.4		--	--		--
	n	3	1	2	1	4	3		1	1		1
	ΣD_g	1.9	0.7	1.1	0.4	2.7	2.4		0.5	1.2		0.7
	D_g	0.8	0.6	0.6	0.4	0.6	0.6	1.0	0.6	0.8		0.7
	S_g	0.4	0.1	0.3	0.1	0.4	0.3	0.2	0.3	0.3		0.1
	n	11	7	20	3	24	10	3	6	3		2.8
	ΣD_g	8.4	4.3	13.8	1.1	15.0	5.7	3.0	3.4	2.5		

D_g = mean effective diameter (μm)

S_g = standard deviation

n = number observed

ΣD_g = sum of effective diameters

Appendix Table 42. Size summary of flyash, salt, lead, metal and carbon aerosols observed on stage 6 of the 16 Nov. 1973 Trout Farm 8-stage Anderson Impactor

Stage-area	Flyash			Lead Compound			Carbon				
	Si-rich	Cs-rich	Metal-rich	Total	Pb	PbAc2(%)	Metal	Salt	Particles	Auto Release	Organic Species
6-Outer	D _g	0.2	0.3	0.3		0.5	0.5	0.7	0.7	1.6	
	S _g	--	0.1	0.1		0.3	--	0.3	0.4	1.3	
	n	1	3	4		3	1	3	4	23	
	ΣD _g	0.2	0.8	1.0		1.5	0.5	2.1	2.8	36.3	
6-Middle	D _g	1.1	1.1	0.9		0.4	0.4	0.4	0.2	2.5	
	S _g	0.3	--	0.4		0.1	0.2	0.1	--	1.0	
	n	2	1	4		1.7	1.2	0.8	0.2	17.5	
	ΣD _g										
6-Center	D _g	0.7	0.9	0.8		0.8	0.7	0.5	0.5	1.8	
	S _g	0.4	--	0.3		--	--	0.3	0.2	1.2	
	n	4	1	5		1	1	2	2	10	
	ΣD _g	2.9	0.9	3.8		0.8	0.7	0.9	0.9	18.3	
Total	D _g	0.8	1.1	0.4		0.8	0.5	0.5	0.6	1.9	
	S _g	0.4	--	0.3		--	0.1	0.2	0.3	1.2	
	n	7	1	5		13	8	7	7	40	
	ΣD _g	5.3	1.1	2.0		0.8	3.9	1.7	3.8	3.9	72.1

D_g = mean effective diameter (μm)

S_g = standard deviation

n = number observed

ΣD_g = sum of effective diameters

Appendix Table 43. Size summary of flyash, salt, lead, metal and carbon aerosols observed on the backup stage of the 16 Nov. 1973 Trout Farm 8-stage Anderson impactor

Stage-area	Flyash			Lead Compound			Carbon		
	Si-rich	Co-rich	Metal-rich	Total	Pb	PbO-Cu(8)	Metal	Salt	Particulates
B-Outer	D _e	2.8		2.8					8.4
	S _d	--		--					7.2
	n	1		1					14
	ΣD _e	2.8		2.8					117.6
B-Middle	D _e	2.0		2.0					6.8
	S _d	--		--					4.4
	n	1		1					22
	ΣD _e	2.0		2.0					149.9
B-Center	D _e	2.8	3.2	3.0		2.8			7.0
	S _d	--	--	0.3		--			3.0
	n	1	1	2		1			14
	ΣD _e	2.8	3.2	6.0		2.8			96.7
Total	D _e	2.8	2.7	2.7		2.8			7.3
	S _d	--	0.6	0.5		2.8			4.1
	n	1	3	4		1			50
	ΣD _e	2.8	8.0	10.8		2.8			364.2

D_e = mean effective diameter (μm)

S_d = standard deviation

n = number observed

ΣD_e = sum of effective diameters

Appendix Table 44. Relative X-Ray Fluorescence Intensities for Stages 3-7 for Trout Farm Anderson Impactor, 16 Nov. 1973, for Outer, Middle and Center Area.

Stage	Area	Elemental Fluorescence Lines Used in Particle Analyses (Integrated Counts)										
		Al/Br	Si	S/Pb ²	Pb(L _α)	Br(K _α)	Cl	K	Ca	Fe	Zn	
3	Outer	1043	9825	250	--	--	--	583	455	544	--	
3	Middle	1774	9760	355	--	--	--	1029	919	896	--	
4	Outer	1894	8858	472	58	--	--	784	844	957	--	
4	Middle	2363	10682	707	67	--	342	1014	1234	1116	--	
4	Center	1798	9588	687	66	--	240	886	1368	1030	--	
5	Outer	1327	7206	1351	222	128	395	614	1164	1002	--	
5	Middle	2193	8359	1472	277	168	375	930	1707	1369	--	
5	Center	1478	5546	1098	251	138	372	525	1032	626	--	
6	Outer	1019	3921	1892	69	29	114	430	668	455	108	
6	Middle	1108	3684	1965	59	27	189	435	626	556	61	
6	Center	1181	3780	1869	115	40	210	438	508	657	95	
7	Outer	931	3384	3362	92	54	260	486	384	535	107	
7	Middle	753	3897	3724	114	51	160	506	337	445	123	
7	Center	855	3845	2666	73	49	216	571	554	382	116	

¹ Total Count = 100K

² Emission produced by sulfur K_α decay and lead M_α decay.

Appendix Table 45. Relative X-Ray Fluorescence Intensities for Two Morphologically Different Areas in a Middle Spot of Stage 7 of the Trout Farm Anderson Inspector, 16 Nov. 1973

Area of Impact Spot	Al/hr	Si	S/Pb	Pb(La)	Br(La)	Cl	K	Ca	Fe	Zn	Ti
Inner	2213 (820) [7.1]	11947 (4425) [38.1]	10492 (3986) [33.5]	369 (137) [1.2]	121 (45) [0.4]	576 (213) [1.8]	1789 (663) [5.7]	1562 (579) [5.0]	1664 (616) [5.3]	400 (148) [1.3]	217 (80) [0.7]
Outer	2083 (771) [10.6]	4236 (1569) [21.7]	9927 (3677) [50.7]	436 (161) [2.2]	209 (77) [1.1]	354 (131) [1.8]	558 (207) [2.9]	496 (184) [2.5]	731 (271) [3.7]	289 (107) [1.5]	243 (90) [1.2]
% Inner/% Outer	0.670	1.756	0.661	0.545	0.364	1.000	1.966	2.000	1.432	0.867	0.583

Total Count = 270K

) = normalized counts to 100K

] = % of total counts

Appendix Table 46. Ratios of Various Elemental Fluorescence Intensities for Stages 3-7 of the Trout Farm Anderson Impactor, 16 Nov. 1973

Ratio	Stage					r_{xy} of ratios
	3	4	5	6	7	
Pb_{LA}/Br_{KA}	--	--	1.72	2.53	1.82	0.113
$(S_{KA} \text{ or } Pb_{KA})/Pb_{LA}$	--	9.72	5.23	23.57	34.97	0.897
$Si_{KA}/(S_{KA} \text{ or } Pb_{KA})$	32.32	15.61	5.38	1.99	1.14	- 0.918
Cl_{KA}/Pb_{LA}	--	4.55	1.52	2.11	2.28	- 0.604
Cl_{KA}/Br_{KA}	--	--	2.63	5.34	4.16	0.563
$(Al_{KA} \text{ or } Br_{LA})/Br_{KA}$	--	--	11.49	34.47	16.59	- 0.211
$Si_{KA}/(Al_{KA} \text{ or } Br_{LA})$	6.95	4.81	4.22	3.44	4.38	- 0.779
K_{KA}/Ca_{KA}	1.17	0.79	0.55	0.72	1.23	0.027
K_{KA}/Fe_{KA}	1.11	0.87	0.71	0.78	1.15	0.008
Ca_{KA}/Fe_{KA}	0.95	1.11	1.30	1.08	0.94	- 0.054
Si_{KA}/Fe_{KA}	13.51	9.39	7.04	6.83	8.17	- 0.768

Appendix Table 47a. Relative X-Ray Fluorescence Intensities for Stages 3-7 for the Trout Farm Anderson
8-Stage Impactor, 14 Nov. 1973

Stage	Elemental Line Intensity (Integrated Counts)									
	Al/Kr	Si	S/Pb	Pb(Ln)	Br(Ka)	Cl	K	Ca	Fe	Zn
3	1320 [9.5](1)	10036 [72.6]	183 [1.3]	--	--	--	775 [5.6]	736 [5.3]	781 [5.6]	--
4	933 [7.7]	8288 [68.3]	657 [5.4]	--	--	--	725 [6.0]	772 [6.4]	755 [6.2]	--
5	1147 [12.1]	5122 [57.2]	1042 [11.0]	166 [1.8]	20 [0.2]	100 [1.1]	389 [4.1]	567 [6.0]	596 [6.3]	31 [0.3]
6	630 [9.8]	2754 [42.8]	1681 [26.1]	265 [4.1]	--	88 [1.4]	236 [3.7]	349 [5.4]	353 [5.5]	82 [1.3]
7	N/A									

(1) [] = % of recorded integrated counts

Appendix Table 47b. Relative X-ray Fluorescence Intensities for Stages 3-7 for the Adams County Fairground
Anderson 8-stage Impactor, 14 Nov. 1973

Stage	Elemental Line Intensity (Integrated Counts)									
	Al/Br	Si	S/Pb	Pb(L _α)	Br(K _α)	Cl	K	Ca	Fe	Zn
3	95 [2.8]	2842 [84.0]	115 [3.4]	--	--	--	136 [4.0]	169 [5.0]	27 [0.8]	--
4	175 [2.5]	5163 [73.9]	200 [2.9]	52 [0.7]	--	--	439 [6.3]	547 [7.8]	412 [5.9]	--
5	435 [6.1]	4186 [58.4]	782 [10.9]	42 [0.6]	--	140 [2.0]	301 [4.2]	840 [11.7]	377 [5.3]	63 [0.9]
6	400 [10.2]	1884 [48.0]	1199 [30.5]	--	--	114 [2.9]	1021 [2.6]	36 [0.9]	136 [3.5]	53 [1.3]
7	555 [7.3]	2356 [30.9]	4048 [53.1]	150 [2.0]	--	--	206 [2.7]	104 [1.4]	135 [1.8]	64 [0.5]

(1) [] = % of recorded integrated counts

Appendix Table 40a. Relative X-Ray Fluorescence Intensities for Stages 3-7 for the Trout Farm Anderson 8-Stage Impactor, 16 Nov. 1973

Stage	Elemental Line Intensity (Integrated Counts)									
	Al/Br	Si	S/Pb	Pb(La)	Br(La)	Cl	K	Ca	Fe	Zn
3	1409 (517) [10.2]	9793 (46) [71.4]	303 (74) [2.2]	--	--	--	806 (315) [2.3]	687 (328) [2.4]	725 (242) [1.8]	--
4	2018 (302) [12.8]	9709 (918) [61.5]	622 (130) [3.9]	64 (5) [0.4]	--	291 (72) [1.8]	895 (115) [5.7]	1149 (272) [7.3]	1034 (80) [6.6]	--
5	1666 (463) [12.1]	7037 (1414) [51.0]	1307 (191) [9.5]	250 (26) [1.8]	145 (21) [1.1]	381 (13) [2.8]	710 (191) [5.1]	1301 (358) [9.4]	999 (372) [7.2]	--
6	1103 (81) [12.6]	3795 (119) [43.3]	1909 (50) [21.8]	81 (30) [0.9]	32 (7) [0.4]	171 (50) [1.9]	434 (4) [4.9]	601 (83) [6.9]	556 (101) [6.3]	88 (24) [1.0]
7	846 (89) [8.7]	3709 (282) [38.3]	3251 (536) [33.6]	93 (21) [1.0]	51 (3) [0.5]	212 (50) [2.2]	521 (44) [5.4]	425 (114) [4.4]	454 (77) [4.7]	115 (8) [1.2]

(1) () - standard deviation for mean intensity for analyzer, middle, and center spot

(2) [] - % of recorded integrated counts

Appendix Table 48b. Relative X-Ray Fluorescence Intensities for Stages 3-7 for the Adams County Fairgrounds Anderson 8-stage Impactor, 16 Nov. 1973

Stage	Elemental Line Intensity (Integrated Counts)									
	Al/hr	Si	S/Pb	Pb(L _α)	Br(K _α)	Cl	K	Ca	Fe	Zn
3	823 [8.7] (1)	6103 [64.8]	251 [2.7]	--	--	94 [1.0]	720 [7.6]	668 [7.1]	761 [8.1]	--
4	817 [4.7]	12137 [69.5]	663 [3.9]	86 [0.5]	--	100 [0.6]	1325 [7.6]	1312 [7.5]	997 [5.7]	--
5	1214 [7.3]	10717 [64.8]	834 [5.0]	197 [1.2]	20 [0.1]	150 [0.9]	828 [5.0]	1485 [9.0]	1032 [6.2]	67 [0.4]
6	712 [6.8]	5744 [55.0]	1461 [14.2]	219 [2.1]	--	218 [2.1]	647 [6.2]	883 [8.5]	543 [5.2]	--
7	300 [3.5]	2016 [23.8]	4200 [49.5]	82 [1.0]	17 [0.2]	160 [1.9]	671 [7.9]	554 [6.5]	415 [4.9]	67 [0.3]

(1) [] = % of recorded integrated counts

Appendix Table 49a. Relative X-Ray Fluorescence Intensities for Stages 3-7 for the Trout Farm Anderson 8-stage Impactor, 17 Nov. 1973

Stage	Elemental Line Intensity (Integrated Counts)									
	Al/Br	Si	S/Pb	Pb(L _α)	Br(L _α)	Cl	K	Ca	Fe	Zn
3	630 [5.1]	9372 [75.4]	200 [1.6]	--	--	140 [1.1]	712 [5.7]	815 [6.6]	557 [4.5]	--
4	673 [6.1]	7729 [70.1]	358 [3.2]	--	--	102 [0.9]	635 [5.8]	997 [9.0]	538 [4.9]	--
5	700 [6.2]	6869 [60.7]	960 [8.5]	56 [0.5]		196 [1.7]	785 [6.9]	1075 [9.5]	672 [5.9]	--
6	800 [10.7]	3037 [40.4]	2266 [30.2]	129 [1.7]	10 [0.1]	231 [3.1]	264 [3.5]	303 [4.0]	430 [5.7]	41 [0.5]
7	540 [8.1]	2058 [30.9]	2319 [34.8]	239 [3.6]	16 [0.2]	173 [2.6]	380 [5.7]	222 [2.5]	500 [7.5]	108 [1.6]

(1) [] = % of recorded integrated counts

Appendix Table 50a. Relative X-ray Fluorescence Intensities for Stages 3-7 for the Trout Farm Anderson
8-Stage Impactor, 21 Nov. 1973

Stage	Elemental Line Intensity (Integrated Counts)									
	Al/Br	Si	S/Pb	Pb(L _α)	Br(L _α)	Cl	K	Ca	Fe	Zn
3	492 [9.1]	3723 [68.9]	102 [1.9]	--	--	160 [3.0]	262 [4.9]	410 [7.6]	252 [4.7]	--
4	600 [8.0]	4754 [63.8]	419 [5.6]	--	--	97 [1.3]	537 [7.2]	545 [7.3]	473 [6.3]	30 [0.4]
5	630 [7.7]	4409 [53.9]	1276 [15.6]	167 [2.0]	19 [0.2]	147 [1.8]	358 [4.4]	682 [8.3]	421 [5.1]	76 [0.9]
6	205 [2.8]	1622 [22.0]	4442 [60.2]	110 [1.5]	8 [0.1]	100 [1.4]	220 [3.0]	259 [3.4]	358 [4.8]	68 [0.9]
7	149 [1.3]	278 [2.4]	10760 [92.1]	93 [0.8]	6 [0.1]	84 [0.7]	100 [0.9]	38 [0.3]	136 [1.2]	--

(1) [] = % of recorded integrated counts

Appendix Table 50b. Relative X-ray Fluorescence Intensities for Stages 3-7 for the Adams County Fairground
Anderson 8-Stage Impactor, 21 Nov. 1973

Stage	Elemental Line Intensity (Integrated Counts)									
	Al/K α	Si	S/Pb	Pb(L α)	Br(K α)	Cl	K	Ca	Fe	Zn
3	605 [11.3]	2752 [51.6]	400 [7.5]	20 [0.4]	--	90 [1.7]	439 [8.2]	655 [12.3]	372 [7.0]	--
4	489 [9.6]	2669 [52.2]	590 [4.5]	--	--	120 [2.3]	300 [5.9]	635 [12.4]	314 [6.1]	--
5	802 [7.8]	4919 [47.9]	2483 [24.2]	34 [0.3]	--	99 [1.0]	196 [1.9]	1047 [10.2]	667 [6.5]	12 [0.1]
6	99 [1.5]	1516 [23.3]	3982 [61.1]	116 [1.8]	--	131 [2.0]	185 [2.8]	226 [3.5]	260 [4.0]	--
7	100 [0.8]	1044 [8.5]	10604 [86.2]	--	--	88 [0.7]	160 [1.3]	210 [1.7]	100 [0.8]	--

(1) [] = % of recorded integrated counts

Appendix Table 51. Observed volume (micro meters³) of particles on the backup filter and stages 0-5

Stage	Particle Type							Total
	Mineral	Flayash	Lead	PbBrCl	Metal	Salt	Auto Emission	
0	18,612	389	--	--	138	--	18	19,157
1	18,461	93	--	--	--	--	5	18,599
2	13,519	532	--	--	--	--	--	14,051
3	693 (90.6) ¹	66 (8.6)	1 (0.1)	--	5 (0.7)	--	34	799
4	207 (85.8)	31 (12.9)	> 1	1 (0.4)	1 (0.4)	1 (0.4)	6	247
5	48 (73.9)	7 (10.7)	> 1	5 (7.7)	2 (3.1)	3 (4.6)	2	67
Backup	2,593	79	--	22	--	--	2665	5,359

¹ Percent of volume, excluding auto emission